

A HISTORY OF CHEMISTRY

BY

F. P. ARMITAGE, M.A., F.C.S.

LATE EXHIBITIONER OF MAGDALEN COLLEGE, OXFORD

ASSISTANT MASTER AT ST. PAUL'S SCHOOL



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was scarcely conceived. The understanding of some of the problems and solutions is not easy ; the mind of a Berzelius is not sounded without resolute effort.

The first two chapters are much compressed. Until the beginning of the seventeenth century the work of the laboratory was purely empirical or guided by a philosophy which may be expressed in a few lines ; modern science has little kinship with that of Geber or Paracelsus. Nor are the labours of Black, Priestley, and Cavendish so difficult of appreciation or of such educative value as to demand much space. But with Lavoisier one enters into the province of the new chemistry with its quantitative methods and reasoned terminology.

• This book is offered to the reader without apology. I hope that whatever its faults may be, the student of chemistry may derive profit by learning something of the mind, the method, the enterprise, and the energy of the great fathers of the science, and be stimulated by their example to become a faithful guardian of his inheritance from the past, and himself a zealous worker for its advancement in the future. It may reasonably be maintained that the subject of these pages should form a necessary part of the mental equipment of every true chemist. The domain of chemistry is so vast and so complicated that much of our information must necessarily be at second hand. And the terms of the chemist—his alkali, his acid, his atoms, molecules, equivalents, his valency and basicity—are each the product of many a life's work. To have used them, and used them often, is not necessarily to have understood them nor to have become emancipated from the dogmatism of the elementary text-book. For the young a little dogma is expedient, and indeed essential ; but for the serious student there can be no substitute for some knowledge of Lavoisier, Dalton, Berzelius, Liebig, Gerhardt, and Kekulé.

It is not the knowledge how this, that, or the other man discovered this, that, or the other substance by some odd chance which makes the history of chemistry worth the

paper it is printed upon ; it is rather the appreciation of how his, that and the other fact, when read acutely, suggested and ratified generalization. Induction, generalization, deduction, are processes to be followed historically, or chemical science will lose much of its significance, and its terminology delude rather than assist the thoughtful inquirer. •Each day brings a new problem to the man of science. The means by which these problems are attacked may be very different from those at the command of our fathers ; but the mind which directs them has scarcely become more acute during the hundred years that have made chemistry an almost exact science. It is well worth while to learn how this mind in its loftiest form regarded and fought with problems which are successively presented to the student during his pupilage and to which his own investigations in every subsequent year will offer the closest analogies.

In conclusion, I would offer acknowledgments and warmest thanks to my friends Mr. G. G. Loane and Mr. T. W. Gould for the care they have expended in watching this volume through the press.

F. P. ARMITAGE.

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P R E F A C E

THAT some knowledge of the history of chemical science is necessary for the true understanding of that science is suggested by the inclusion of historical data in all the best chemical text-books of the day, organic, inorganic, and physical. Necessarily it is the larger books only that are furnished with such details, and these books are not in every one's hands; the historical notices are either isolated and often of merely antiquarian interest, or, when gathered into a continuous narrative, must sacrifice liveliness to compression. The complete histories of the science are very large, and written in a foreign language, or, like that of Ernest Meyer, are so excessively comprehensive as to conceal the development of main issues from those whose opportunities for study are limited.

I trust that I have told and transcribed enough in these pages to enable the reader with some thought to gauge the niceness of experiment, the rigour of logic, the inevitability of conclusion, which have made the chemistry of to-day. So much of what follows is based on the classical works of Hermann Kopp and Hoefer, and affected by the later work of Ernest Meyer, that the references given to these must by no means be taken as complete. In all cases, where possible, authorities have been made to tell their own story. The nomenclature and notation used are those of the times described. To have modernized them would certainly have simplified reading, but would have suggested that a most powerful instrument for progress existed in times when it

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A HISTORY OF CHEMISTRY

CHAPTER I

FROM EARLIEST TIMES TO THE DOWNFALL OF "IATRO-CHEMISTRY"

A MOMENT'S thought on the nature of chemical facts convinces us that their recognition was coeval with the dawn of human intelligence. Even during that stage of transition which separated him from the brute creation, man must have appreciated the beneficial or harmful effect of many naturally occurring substances.

It was most probably in Egypt that these facts were first intelligently sought after and grasped, for it is in the records of the Egyptians that we first find traces of any definite aim—that, namely, of transmutation. Indeed, the very name "chemistry" is evidence in favour of accepting Egypt's priority as the home of chemical science, for it is from her ancient appellation "chemia" that the word appears to be derived, though it is not mentioned as signifying a definite science till the first half of the fourth century. Yet some form of the word was meanwhile applied in Arabia to the body used in transmutation, the philosopher's stone. From Egypt the science spread westward to Rome and beyond.

There is evidence of the Chinese also having paid attention to the facts of chemistry at a very early date, though their isolation prevented any effect of their discoveries being felt outside their own country.

Egypt the
birthplace
of
chemistry.

Chemical knowledge at the beginning of our era.

At the beginning of our era chemical knowledge did not extend beyond the manufacture of such articles as glass, soap, dyes, and the preparation and purifying of such easily reducible or naturally occurring metals as gold, silver, iron, lead, and copper. Still, the manufacture of glass and soap presupposed that of potash and soda, and the fixing of dyes necessitated some knowledge of alum. Other preparations too were used for medicinal purposes, verdigris and white lead being employed in salves. Iron had been long recognized as a valuable tonic, burning sulphur as a purifying agent. All testified to a considerable power of empirical observation.

As yet no attempt at systematizing the knowledge gained.

Nevertheless as yet there had appeared no attempt at systematizing the knowledge of chemical facts so gained. Systems of philosophy dealing with the ultimate composition of matter there had long been, but these exercised no influence on the work of the laboratory. Of these philosophies one only is to be considered here, that which owed its general acceptance, if not its origin, to Aristotle.

Aristotle's theory of the elements.

Aristotle maintained the four elements, earth, air, fire, and water, each of which was distinguished by two specific properties, earth and water combining that of cold, fire and air that of heat with dryness and wetness respectively. One was not to attempt the isolation of these elements; they were rather to be considered as abstract qualities exhibited by one primordial matter. The immediate influence of this theory on the chemistry of the ancients was small, yet it did much to prepare men's minds for the reception of a belief in transmutation, and proved so of much value. It was not till the middle of the seventeenth century that its sway was finally rejected.

We thus find at the beginning of our era a considerable knowledge of chemical facts, and a theory which, though independent of these facts, yet joined with them in focussing men's minds on one cardinal issue, the transmutation of metals.

Alchemy.

Our knowledge of the genesis of alchemy is small; the oldest records, those of the Egyptian papyrus at Leyden, only

go back to the third century, and merely consist of a number of recipes, couched in symbolic and unintelligible language, for the preparation and purifying of various metals, with information on the art of glass-making, gilding, and the duplication of gold. The mysticism in writing was indeed a necessity of the time, for it was a heinous crime to reveal secrets of alchemy or metal-working to others than the sons of kings, or priests.

But we require no records to understand how many and obvious are the chemical phenomena which might well have suggested a belief in the possibility of transmutation. The deposition of metallic copper on iron immersed in its solution must have converted many, and to those still doubtful even more direct evidence was afforded by the discovery of gold and silver nodules after cupellation of chance specimens of lead. Finally, a firm belief in Aristotle's doctrine of the elements, the ocular demonstration of Egypt's colossal wealth, and a rooted prejudice in favour of every species of occultism, would remove from the most sceptical the possibility of doubting the testimony afforded by inscriptions on their columns.

Evidence conducive to a belief in transmutation.

The devastation of the temple of Serapis by the Romans brought the sacred art of alchemy to Athens, where its investigation was suppressed by Justinian in 529. Constantinople became then the centre of its activity, and it was by virtue of their commerce with this city that the Arabs became acquainted with the idea of transmutation in the eighth century.

Spread of alchemy.

Any knowledge that we possess of the manner of research during this long period is derived from a number of writers, the earliest of whom lived at the beginning of the third century. These writings, like those of the papyrus mentioned above, are to a great extent incomprehensible. "The moon is pure and divine when one sees the sun shining on its surface." This, the statement of Zosimus, is somewhat enigmatical, but yet more luminous than was customary, and seems to refer to the sudden appearance of metallic brilliancy during the final stage of the cupellation of silver.

Manner of research in early times.

Such classification of bodies as there was among the

Classification

among the Egyptians. Egyptians was based on modes of preparation, rather than on chemical properties. Gold, silver, iron, lead, lapis lazuli, emerald, all bodies in fact distinguished by glance or rarity, or which were produced by the agency of fire, were brought together under the one heading "metal." Gold and silver were regarded as alloys, and indeed such was often the case, for Nero was the first sovereign who seems to have demanded pure gold. Lead with the Egyptians occupied the same position as mercury with the later alchemists; it was the hermetic body *par excellence*.

The philosopher's stone. The fact that a small addition of some substance induced a definite colour in a large mass of glass or metal had already led to a belief in the philosopher's stone, a substance whose addition to some base metal would convert the whole into silver or gold. But it was not till later that its full powers, transmuting and medicinal, obtained recognition.

Scientific activity in Spain. The eighth century saw the planting of scientific culture in Spain, brought about through the founding of an Arab Caliphate at Cordova; whence sprung those famous universities of Cordova, Seville, and Toledo. It was at Seville, and in all probability during the second half of the eighth century, that the physician Geber carried on his great work. In his writings, which, contrary to the then established code, are mostly quite intelligible, are described for the first time the preparation of sulphuric acid by the distillation of alum, and of nitric acid by the action of this sulphuric acid on saltpetre. By the addition of nitric acid to salmiac he obtained the so-called aqua regia. Geber, moreover, prepared potash and soda by the incineration of tartar and sea plants respectively, and by their action on his acids was led to the discovery of many new salts. He possessed an extensive knowledge of the oxides and sulphides of various metals, and described the whitening of copper by fusion with white arsenic; and also the purification of sulphur by solution in alkali and subsequent precipitation with vinegar. He enriched chemistry by his observations on the amalgamation of many metals by

mercury, and particularly by his description of new and improved forms of apparatus. Especially was this the case with regard to those required in distillation, filtration, and cupellation.

Not only was Geber a pioneer on the practical side of his science; his endeavour to give the pursuit of alchemy some theoretical foundation resulted in a theory of metallic composition which, in a more or less modified form, remained the common basis of alchemical labour till finally shattered by Boyle. At the beginning of our era Dioscorides had spoken of mercury as a necessary component of all metals; the only other component Geber now decided must be sulphur. One was not, however, to regard the mercury and sulphur, so well known in the concrete form, as the elements in question; rather, were these latter of an abstract nature—metaphysical substances: mercury, something which conferred glance, fusibility, and metallic properties in general; sulphur, that which conferred alterability by fire. And this conception differed from all previous in that it was based on observation. The power which mercury possesses of dissolving many metals was due to an affinity, a likeness, between them, and the production of a veritable tin by the combination of mercury with lead was further indication of the common genesis of metals; again, the sulphurous smell observed on the calcination of tin was very cogent evidence of the presence of sulphur.

The breaking up of the Caliphate of Bagdad in the middle of the thirteenth century, with the subsequent attacks of Christendom on its Spanish dependencies, proved the death-blow of Arabian science. Yet, though none of its votaries had ever approached Geber in originality of thought or wealth of discovery, they had carefully spread the good seed, and spread it, too, on rich ground. The Spanish universities had been sought diligently by aspiring students from England, France, and Germany, and it was to their hands that the welfare of the science was now worthily entrusted.

The thirteenth century was especially rich in alchemical

Geber's
theoretical
views.

Arabian
science
ceases in
the middle
of the
twelfth
century.

Magnus,
Bacon,

Villanovanus, and Lully. labours. Among those who worked hard to impress the popular mind with a belief in the power of their art they stand out four very distinctly. These, Albertus Magnus, Roger Bacon, Arnaldus Villanovanus, and Raymond Lully, during their wandering and persecuted lives had little opportunity to extend the knowledge of purely chemical facts, yet something they did. Indeed, the discovery of gunpowder has been ascribed to Magnus, though it is more than probable that he derived his information from one Marcus Græcus, a Byzantine writer of the eighth century, who left a recipe for the preparation of an improved form of Greek fire. Magnus knew of the separation of silver from gold by treatment with nitric acid, and also of the sublimation of sulphur and arsenic on strongly heating various ores. Bacon, too, prepared arsenic from its sulphide by the action of iron, and was the first to distinguish between alum and vitriol. Villanovanus recognized the inflammability of alcohol, and knew how to prepare it from red wine by distillation, an art in which he was well advanced; while Lully showed how the spirit might be dehydrated by distillation over potashes.

Basil Valentine. No other name of importance strikes us in the history of this time, till in the fifteenth century we are met by that of Basil Valentine, whose genius prepared the way for the new chemistry, a chemistry which was to have as its object, not the transmutation of base metals into gold, but the preparation and intelligent prescription of medicines. Let us halt a while that we may the better gauge the merit of his activities.

General effect of the pursuit of alchemy on chemistry. During all these centuries the evolution of chemistry as a science had necessarily been very slow, for the chief aim of its exponents, the production of gold, was incompatible with real progress. No intimate knowledge of the composition of the various preparations used seemed necessary to a successful issue, and in consequence none was striven after. The prevalent belief in transmutation bore on this point still more directly; one must remember that while the production of the mild alkalis by the incineration of plants had been long known,

few regarded them as present in the original substance. A few metals, however, as antimony, zinc, and perhaps bismuth, had been added to the list, and their actions on various acids observed; but this was all. Yet one marks a notable innovation in the employment of the balance which had been instituted by law in all processes of cupellation and cementation of the noble metals. How little indeed the prosecution of hermetic art could necessarily have to say to the advance of chemical science will appear if we consider the nature of its methods a little more closely than has as yet been feasible.

Almost the entire interest of the adept was centred in the preparation of the philosopher's stone. According to Geber, before transmutation was complete, his three so-called medicines had to be applied. The first of these produced merely a temporary change in the base metal, the second a partial transmutation; but it was only after the addition of the third, the great elixir, the philosopher's stone, that a real consummation was attained. For the preparation of this last every conceivable substance was brought into requisition; fortune might favour any chance fusion or mixing. After Geber the procedure of alchemy became much simpler. The stone, or rather powder, red or white, according as gold or silver were to be produced, was now thrown on the metal—lead or mercury was preferred—the whole worked together, and finally poured out as pure gold or silver. It was Lully who ascribed the greatest powers to the stone; were the sea of mercury, by means of this stone he would convert it into gold.

The character of alchemical labours.

Geber had not regarded his great elixir as endowed with any peculiar medicinal virtues, but in the thirteenth century we find Villanovanus and Lully extolling its sovereign powers against all human ills, though the former was sufficiently modest to allow more time for the cure, the greater lengths the disease had run. Villanovanus even regarded gold in solution as a medicine, potent for good.

The philosopher's stone as a universal medicine.

Yet it was not till the seventeenth century had set in, says the alchemistic historian, Schmieder, that alchemy reached its zenith. He will admit a possibility of doubt as to the

Alchemy after 1600; its religious element.

credibility of the adept's work in times gone by, but the numerous transmutations of Alexander Setonius Scotus performed between the years 1602 and 1604, in presence of chemists, medical men, and city magnates, were beyond dispute. But the history of alchemy in these later times concerns chemistry little. The once sacred art had become the trade of men, the majority of whom were mere charlatans, with often good cause to rue their temerity in deceiving too credulous patrons. Germany was overrun with these depredators, whose small princes found their finances in so evil a state that they were led to look with favour on the seductive art, and then, after wasting their substance in fruitless experiment, to wreak their fury on its pretended adepts.

Lully's writings had made it a matter of faith among alchemists that a man must be predestined to favourable results. So there was found reason in their custom of offering up prayers before each experiment, the relic, perhaps, of a time when the duration of an operation was estimated by the number of paternosters and aves that could be repeated the while. Analogy, too, was found between the transmutation of metals and that of the human body; life, death, and resurrection thus came to be regarded as mere alchemistic feats of a superior order.

The alkahest.

Of a similar nature with the belief in the philosopher's stone was that in a universal solvent, Valentine's alkahest, a belief which, however, only dates from the time of the English alchemist, Ripley, in the fifteenth century. To the alkahest were ascribed extraordinary medicinal properties in addition to that of bringing the most refractory substances, even gold and sand, into solution. It was variously described as a liquid and a solid, and was at different times supposed identical with hydrochloric acid, acetic acid, and potashes.

Valentine and his work.

In the work of Valentine we begin to recognize the leading tendencies of the following era. Who he was, where he lived, and when, remain enigmas; still, tradition and the internal evidence of his writings lead one to accept the second half of

the fifteenth century as his period. An edition of his works was first published during the early part of the seventeenth century. Kopp is of opinion that the whole may be considered a forgery, though, indeed, he allows it difficult to understand why Tholde the publisher, if he were the culprit, should have given so many new facts to the world under an assumed name. In the famous *Triumphwagen des Antimons*, the first definite monograph on any element, are found accurate accounts of the preparation of metallic antimony by many different methods; of its sulphide, chloride, and oxide. The application of antimony sulphide to the purification of gold from admixture with other elements is also mentioned, and a solution of the metal is highly extolled as a medicine. Valentine was the first to mention definitely bismuth and tin, and he showed considerable analytical skill in demonstrating the presence of gold in many of the common metals, and in so exposing some of the alchemistic cheats of his day. And we have, moreover, to thank him for the discovery of hydrochloric acid, which he prepared by the action of vitriol on ordinary salt.

Valentine's philosophy of composition was peculiar; he allowed but three elements, the sulphur and mercury of Geber, and salt, by this latter understanding a principle of stability and non-volatility under the action of fire; and not only did he find support for this philosophy in his knowledge of the metals, but of all other matter, organic and inorganic.

Pharmaceutical chemistry had hitherto made little progress; some working theory of disease was needed as a spur. The ancient school of Galen still retained its authority, and chemical preparations were only used externally. It is true that at times the Greek physicians had ordered iron rust and chalcantus (probably a mixed sulphate of iron and copper) to be taken internally; but oxide of zinc, arsenic, and lead preparations were only used in salves and ointments. It must be mentioned, too, that the Arabs between the tenth and twelfth centuries had introduced the practice of distillation, by means of which the active principles of roots and herbs were isolated, and had recommended the use of the latter in place of the

Valentine's three elements.

Chemistry and the art of healing.

natural product. Beyond this, however, there had been no advance. But Valentine brought change. Relying solely on experiment and observation of the medicinal effect of his preparations, he passed over the established school with contempt. He insisted on, and, by his successful prescriptions of antimony and mercury salts, to some extent demonstrated the fact, that the word "poison" is truly but a relative term.

Valentine's work the precursor of revolution.

Valentine's work was the natural precursor of revolution; vicious or not, it raised issues which were paramount. At all times, to the majority, health of body has appealed more strongly than wealth of pocket. Where the philosopher's stone, the alkahest, and soluble gold had all failed, a reasoned prescription of chemical compounds might succeed. With Valentine's successor, Paracelsus, there begins a new school of chemistry.

THE PERIOD OF IATRO-CHEMISTRY (1493-1627)

Paracelsus, 1493-1541.

Paracelsus was born at Einsiedeln in Switzerland in 1493. Travel alone would satisfy his restless disposition, and it was not until he had visited almost every European country that he again appeared in his fatherland guised as a doctor. During his travels he had acquired a most extensive knowledge of chemistry, and was now determined to use this in his medical practice. He performed many wonderful cures, but not without becoming embroiled with the civil authorities, owing to his unorthodox prescriptions. He was driven forth, and, after still more extended wanderings, died in miserable circumstances at Salzburg in 1541.

Paracelsus' theoretical views.

It was a new theory which led to the scientific pursuit of alchemy; it was again a new theory which enabled chemistry to shake off the trammels of self-interested empiricism. Accepting Valentine's philosophy of three elements—mercury, sulphur, and salt—and, like him, reading this into all matter indiscriminately, Paracelsus was able to give a theoretical basis to his sense of pathological phenomena. The animal body was a chemical compound of definite composition, and well-being or

sickness was determined by the proportions in which the three elements were present; yet not wholly, for his pantheistic conception of life demanded the presence of some spiritual entity—Archeus, he called it—which should preside over the function of digestion. Should the sulphur increase in quantity, fever and plague would result, while accumulation of mercury or salt would be followed by paralysis or dropsy. On the state of health or activity of Archeus depended the excretion necessary to soundness of body. As with Geber and Valentine, so with Paracelsus, the three elements were not so much definite substances with definite physical properties as abstractions, suggestive of qualities possessed in eminent degree by mercury, sulphur, and salt respectively. His statement, therefore, that there are as many mercuries, sulphurs, and salts as there are organs in the human body is readily understood.

The science of chemistry was now to be restricted to the preparation of medicines, by the action of which the composition of an ailing body might once more be brought to its normal state. Paracelsus' Pharmacopœa included mercury in its metallic state and also in solution; lead, antimony, and iron preparations; also milk of sulphur. Arsenic was only to be applied externally.

Chemistry to be the handmaid of medicine.

The empirical knowledge of Paracelsus was considerable; his criterion of a metal was ductility, and he was therefore led to separate metals from half-metals, as he termed zinc and bismuth. He considered that the difference between alum and vitriol came from the one being a compound of earth, the other of metal.

Paracelsus' empirical knowledge.

While Paracelsus was pressing his doctrines on all sides, and endeavouring to lead chemistry into a new channel, another, Agricola, was quietly at work among the mines of Saxony, utterly indifferent to all but the advance of his science. It is to Agricola's systematic observations that we trace the beginnings of the science of mineralogy. In metallurgy, also, he was a pioneer, the first to give a clear and succinct account

The work of Agricola, 1494-1555.

of the preparation of many metals. He taught the condensation and purification of sulphur given off during the roasting of many ores, the separation of silver from gold by means of nitric and sulphuric acid, the preparation of such bodies as salt, alum, and saltpetre on a large scale. The apparatus described by Agricola and employed by him for the smelting and testing of ores were still in use at the end of the eighteenth century. Agricola stands out solitary among the men of his time as one pursuing chemistry from pure love of the science; his work had no other aim than the increase of knowledge.

The fortunes of the new school of medicine after 1541. Libavius and Sala.

The death of Paracelsus saw the beginnings of a spirited contest between his disciples and the adherents of Galen. The former, lacking the genius of their master but none of his assurance, wrought such havoc by their indiscriminate prescription of the new medicines, that the authorities of Paris passed, in 1566, a stringent edict forbidding their use. Notable voices were raised against their excesses; Libavius and Sala, though embracing the main principles of the new chemistry, did nevertheless endeavour to separate true scientific doctrines from a mysticism and seeming charlatanism which marred the writings of Paracelsus. Their practical work, too, was conceived in a manner more in accordance with honest intent. Thus Sala investigated the causes of reactions, showing how no fulminate of gold was produced unless alcohol were present, while Libavius noticed that oil of vitriol prepared as heretofore and the liquid obtained by the action of nitre on sulphur were one and the same substance. Moreover, Libavius, as the author of his book *Alchymia*, did much to spread abroad that full knowledge of known facts which could alone bring disillusionment.

Van Helmont, 1577-1644.

A far more considerable task fell to the lot of Van Helmont. Born in Brussels in 1577, Van Helmont early joined himself to the school of Galen. Dissatisfied, he turned to the doctrines of Paracelsus, and soon became their firm adherent. His mind was saturated with mysticism, and his arrogance almost equalled that of his preceptor. He was somewhat

credulous too, as we gather from his believing himself the possessor of a small quantity of the stone of proved virtue, his conviction that dirty linen packed in a vessel with flour would in time produce mice, and that a toad's bones applied to an offending part was a certain alleviator of pain. Yet it was this man who, by his views on the active juices of the stomach, laid the foundation of the first consistent theory of digestion, and, by his experiments on gases, introduced a new branch of chemistry. We have already come to the second stage of the iatro-chemical school.

Helmont's conception of the elements differed from that of Aristotle and from that of Paracelsus. To him fire was no element, for he considered the substantial part of flame as mere ignited gas; neither could he regard mercury, sulphur, and salt as the components of the animal body, for none of these substances were to be detected in it. On the other hand, water was everywhere and in everything. A vegetable placed in water with a weighed quantity of earth increased vastly in weight; yet nothing of this could come from the earth, whose weight remained constant throughout the experiment. Obviously some of the water must have changed to leaf and stem. Again, fishes fed on water alone lived and grew fat; their flesh, and probably that of all living creatures, must have come from another transmutation of the one element water. But this maintenance of the all-sufficing power of water exerted little influence in the ever-widening circle of scientific activity; masters in the iatro-chemical school had no time to philosophize; the activities of the natural juices engrossed their whole powers, and any question as to the ultimate composition of these seemed lacking in point.

Till Van Helmont's time little or nothing was known concerning gases. It is true that Pliny had spoken of "spiritus," which possessed properties different from those of ordinary air; of emanations from the ground, some of which were combustible, others suffocating. But even Valentine had not advanced beyond regarding all such as common airs with

Helmont's
one ele-
ment,
water.

Helmont
and the
chemistry
of gases.

differing impurities. The evolution of gas on throwing oil of vitriol over iron had appealed to Paracelsus as a mere breaking out of air. Helmont changed the whole aspect of the question, and this too without the aid of any apparatus by which to collect and examine. In his writings the word "gas" occurs for the first time, a word he perhaps derived from the German "Gischt," the foam which appears on fermentation; and as such he classed all those emanations which could not be brought into the liquid state. Of gases there were two varieties, "gas sylvestre"—so he termed carbonic acid or other gas which extinguished a light and was unbreathable—and "gas pinque," which signified those with a combustible nature. He mentions burning, fermentation, putrescence, action of acids on metals or chalky substances, as phenomena accompanied by the evolution of gases, and remarks on the great quantity of "gas sylvestre" to be found in the Grotto del Cane at Naples. Vapours were to be distinguished from gases in that they might be liquefied, a distinction which held good for centuries.

Helmont's
observations on
combustion com-
plementary to
those of
Rey.

Van Helmont had noticed that when bodies underwent combustion in air, the volume of the latter decreased; an observation which was complementary to that of his contemporary, Jean Rey, who maintained that the increase in weight of metals on calcination was due to absorption of air. Rey had endeavoured to prove that air is a material body by comparing the weights of flasks filled with it under varying pressures, but his conclusions met with little consideration from his contemporaries or successors.

Van
Helmont
Neo-
Paracel-
sian.

Though from many points of view an ardent Paracelsian, Helmont broke away somewhat from this school when he came to consider physiological and pathological phenomena. The presence of mercury, sulphur, and salt in the body was unproven, whereas it was certain that the stomach contained an acid secretion and the duodenum one that was alkaline. Helmont made the most of these facts; digestion, he said, was due to a fermentation induced by the presence of acid, and this fermentation ceased when the acid food was neutralized by the

alkali of the duodenum. Should complete neutralization not occur, disease would result, only to be met by the prescription of alkalis or acids according to its nature. Helmont could not, however, throw off his belief in the "Archers," so it was to it that preponderance of acid or alkali was attributed.

The narration of Van Helmont's valuable contributions cannot end here; for his views on the composition of substances also were far in advance of any of his predecessors. The production of a body differing in appearance and properties from its parent substance or substances had been to them a new creation; the addition to this parent substance of one or more bodies had been necessary, not because certain of their components were to appear in the composition of the new substance, but to induce its creation. And such views had reigned supreme even in the mind of Paracelsus. The precipitation of copper on iron had been to him the deposit of a new metal. Helmont, on the other hand, maintained the unalterability of a metal even on solution, a belief which, though propounded so early as 1477 by Norton, had never met with general recognition. Helmont further made a statement, based on quantitative experiment, that if one body combines with another and is then precipitated, the weight so obtained is equal to that originally taken. He had found that sand, fused to a glass with potash and again precipitated by addition of acid, lost nothing in weight.

Helmont's
enlight-
ened views
on the
nature of
com-
pounds.

The knowledge of the composition of chemical compounds was still further extended by a contemporary of Van Helmont, Johann Rudolph Glauber (born at Karlstadt in 1604), who, while adhering to the Paracelsian medico-chemical doctrines in their entirety, maintaining stout championship of alchemy, the alkahest, and the marvellous powers of potable gold, enriched chemistry in an eminent degree by his discoveries. In attacking this question of the composition of bodies, Glauber began by considering the conditions under which certain salts were produced, and the products of their mutual decomposition. Instead of preparing metallic chlorides as heretofore, by heating the metal with sublimate, he treated the

Increasing
knowledge
of the
compound.
The work
of Glau-
ber, 1604-
1668.

metal directly with hydrochloric acid, and hence concluded that the salt so obtained was merely a solution of the metal in the acid. This was a convincing blow to the time-honoured belief that the mercury of the sublimate had entered into the composition of the resulting chlorides. Moreover, Glauber prepared hydrochloric and nitric acid by the action of sulphuric acid on their salts, recognizing that the established method of distilling these salts with iron vitriol depended on the previous formation of free sulphuric acid; and by acting on these various acids with the alkalis, he obtained many new substances, among which was his *sal mirabile*—ordinary sodium sulphate—in which, as he believed, lay extraordinary medicinal virtue.

The idea
of an
affinity.

The combination of acids with metals or alkalis was ascribed by Glauber to a certain associative tendency, "*Gemeinschaft*," as he called it. The decomposition of ordinary salt by oil of vitriol, of salmiac by chalk and potash, was due to the superior attraction of one of the salt components for the decomposing medium. He further explained rightly the double decomposition of antimony sulphide with corrosive sublimate. These were novel ideas. Glauber never employed the word "affinity," though it was already the property of chemical literature, for long before, Albertus Magnus, when considering metallic sulphides, had spoken of combination depending on an affinity between the sulphur and metal. Hippocrates, in the fifth century B.C., had urged as a dogma that like combines with like, and Geber had this in his mind when, generalizing from the combination of most metals with mercury, he assumed the latter to be a primal element. Magnus's statement was but an echo of the same thought, for sulphur too at his date was regarded as an equally necessary component of metals.

Other
contributions of
Glauber.

It was Glauber who discovered the presence of acetic acid in the distillate from wood, who pointed out how this body might well be substituted for vinegar, who did so much to further the arts of dyeing and glass-staining, and, by his writings, to demonstrate the folly of Germany in neglecting her own raw mineral wealth.

The influence of Van Helmont's theory of physiological action is easily discernible in the teaching of his contemporary, De la Boe Sylvius. This man, whose work brought the iatro-chemical school to its zenith, was born at Hanau in 1614, and died while Professor of Medicine at Leyden in 1672. Though a firm believer in the truths of alchemy and the philosopher's stone, he lent all his energies to the fusion of medicine with chemistry. Sylvius believed the phenomena of life to be dependent merely on a cycle of chemical changes. As with Helmont, so with him, the acid or alkaline character of the digestive juices was of supreme importance to the health of the body; but he differed from the former in excluding all supernatural agencies from his system; Archeus was no longer to preside over digestion. Digestion began in the mouth, where the food came in contact with the saliva, and was only completed in the duodenum, where the food met the acid pancreatic juice and the alkaline gall. The preservation of a correct proportion between these fluids was all-important, for on this depended the temperature of the body, according as the acid or alkaline fluid was predominant, there was experienced cold or heat. By the action of the gall and pancreatic juice on the half-digested matter, chyle was produced, and this, together with blood, reaching the heart in a slightly acid condition, there met other blood impregnated with alkaline gall; there was effervescence with evolution of that heat which warmed the body. Notwithstanding these strange doctrines, Sylvius was able to appreciate the analogy between respiration and burning; moreover, he discriminated between venous and arterial blood, and rightly referred the red colour of the former to its combination with air.

De la Boe
Sylvius,
1614-
1672. His
theory of
digestion
and ani-
mal heat.

The last iatro-chemist of any note was Otto Tachenius, a disciple of Sylvius. Tachenius' contributions to our practical knowledge of the science far surpass those of his master. He was convinced of the existence of the alkahest, and believed he had found it in his acetic acid, prepared by distilling verdigris. His great work had, however, to do with analysis. Hitherto the use of reagents was practically unknown. At the

Otto
Tachenius
and wet
analysis.

beginning of our era Pliny had certainly described the employment of a tincture of galls in detecting iron adulteration of verdigris, but this was an isolated instance. The general method of discovering such adulteration was rather to observe whether one portion of a supposed homogeneous substance was less soluble than another—a method applied by Libavius to the analysis of natural waters so late even as the beginning of the seventeenth century. Colour, taste, and smell had long remained the distinguishing traits of a salt, and the prevailing belief in transmutation had stifled all attempts at a more intimate knowledge. But the opinions of Van Helmont and Glauber on the permanence of a metal had prepared the way for sounder views, and we find Tachenius laying stress on the significance of the colour of the precipitate produced by addition of gall extract to copper, lead, and iron solutions. Moreover, he showed how a solution of common sublimate is affected differently by solutions of fixed and volatile alkalis. His superior analytical acumen enabled him to judge correctly on various disputed points; thus he showed that iron taken inwardly was not excreted in the urine. Like Valentine, he carried war into the camp of the alchemists. His experimental demonstration that lead, on oxidation to minium, increases in weight by one-tenth, marked a sense of the quantitative method.

Tachenius' definition of a salt.

From the solution of silica by fusion with potash Tachenius concluded that the former must be of an acidic nature; likewise the change produced in fats by the action of alkalis was suggestive of these fats containing some hidden acid, and he was led by these and analogous facts to define a salt as a compound of an acid with an alkali.

Conclusion of the iatro-chemical period.

Tachenius was the last of the iatro-chemists. Their work was done. They had preserved the seed of a real science through a troubled and unenlightened period, while their often fantastic speculations had caused no inconsiderable additions to the stock of chemical facts. As this period approached its close, a remarkable change became noticeable. No longer

were vague speculations on the nature of elements and chemical change accepted as dogmas. Men were slowly discovering that a theory, to be helpful, must be based on experiment, and must depend for its general recognition on practical verification, a vindication of the inductive method which was at last becoming general. But already the superstructure of definite fact was too weighty for its feeble theoretic foundations. With many the belief in the practicability of alchemy had been long extinct, and the iatro-chemical system had never been very stable. It only required, then, an acute and critical mind, aided by exceeding practical skill, to demolish the whole edifice and lay the foundations of a new, one based on facts alone, independent of this, that, and the other philosophy alike. Metals and their compounds had been ripe material for the investigation of generations of alchemists, apparatus had been conceived with which to attack them, and from the crucible had issued new elements and new compounds. The fusion of chemistry and medicine had resulted in the birth of organic chemistry; and the application of the most cultivated minds of the period—those of the medical fraternity—to the problems offered by chemical phenomena had resulted in knowledge which had gradually led to some definite idea of analysis, of affinity, of chemical composition, and, what indeed was the parent of all, a recognition of the unchangeability of the metallic nature. Yet any conceptions there might be of the elements, the ultimate components of matter, were utterly vague, based as they still were on the time-honoured theory of Aristotle, modified in greater or less degree by the writings of Geber, Paracelsus, and Van Helmont. A rigorous examination of this vexed question was required before the new chemistry, the science of the composition of bodies, could gain firm foothold, and it was just this which enabled Boyle, after clearing the ground of the corpses of alchemy and iatro-chemistry, to point out the only true road to progress, the road guarded by diligent experiment and stringent induction.

CHAPTER II

FROM BOYLE TO LAVOISIER AND THE ESTABLISHMENT OF THE QUANTITATIVE METHOD

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HITHERTO the inducements to a study of chemical fact had been successively a belief in transmutation, and a trust in the efficacy of heroic medicines prepared in the laboratory. But from the middle of the seventeenth century onwards another aim transpires in the writings of the masters; the sciences were to be pursued for their own sakes, and the discovery of truth was to be the sufficient reward of a real philosopher.

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As we approach our own times, it grows increasingly difficult to define historically the successive phases of chemical science. The founding of scientific societies and the consequent wide dissemination of scientific literature provided ever-accumulating data for the discussion of old and the initiation of new theories. In consequence, firm allegiance to any one school of thought was not to be expected, nor was it found. Yet there was one problem which engrossed the attention of almost all chemists during the seventeenth and eighteenth centuries, and this was the explanation of fire and the phenomena caused by fire. Though here scarcely any two philosophers were agreed in their conclusions, their modes of arriving at them showed marked similarity. The qualitative side of phenomena alone was considered, the quantitative being hardly appreciated. This period, from Boyle to Lavoisier, may be described as that of Qualitative Chemistry. It was a time rich in generalization, for just as fire was to be explained by the assumption of one general principle, phlogiston, so the general properties of acidity and causticity were to be regarded

as conferred by one fundamental acid and one fundamental alkali respectively.

Robert Boyle was born in 1627, and died in 1691. He was Irish by extraction, but spent the greater part of his life in England, quietly devoting himself to the study of natural science and to the furtherance of many philanthropic schemes.

Boyle,
1627-
1691.

Boyle's most lasting service to natural philosophy was perhaps his practical demonstration of the value of the Baconian system; for, though a most able experimenter and astute observer, he appears to have been somewhat lacking in the power of generalization. His work was destructive rather than constructive. His most famous contribution to chemistry, the *Sceptical Chymist*, appeared in 1661, and contained an attack on both the Aristotelian doctrine of the elements and that initiated by Geber. He maintained that nothing which could be further decomposed was to be considered elementary, and that certainly none of Aristotle's elements fulfilled this condition; earth, for example, was resolved into many different substances under suitable treatment. As to Geber's doctrine, he asks whether, since mere inflammability constitutes the essence of the element sulphur, just as the contrary in conjunction with any taste constitutes a mercury, a multitude of substances which, while agreeing in this minor detail, disagree in others more considerable, are to be classed together under the name of one common principle.

The
*Sceptical
Chymist*
and the
nature of
elements.

Boyle disputed the belief in the dissociative power of heat, showing that its effects were often very different, according to the conditions of the experiment; moreover, he was disposed to believe that these effects were the result of an altered disposition of a body's ultimate parts rather than of their absolute isolation. He was of opinion that all bodies were composed ultimately of one primordial matter, and that the properties of any particular substance depended on the motion and mutual attraction of its smallest particles; that in addition two substances, on mixing, would undergo change only when the component parts of the first had less attraction for one

Chemical
effects of
heat. "A
corpuscu-
lar theory
to explain
combina-
tion.

another than for those of the second. This corpuscular theory he applied to the air, which he compared to fleeces of wool, whose density increased in the lower layers, owing to the pressure from the fibres above. Boyle gave, indeed, much thought to this question of the surrounding atmosphere, and drew up a scheme for its thorough investigation, the only practical issue of which, however, was the proof of a something in the air which was destroyed both by respiration and combustion. He was aware that lead on calcination gained in weight, but, instead of referring this to its proper cause, suggested an absorption of igneous particles.

Boyle's wet analysis. Tachenius had done much to show the practicability of wet analysis; Boyle was successful in systematizing and adding to his results. He showed how various plant juices were differently affected by acids and alkalis, and how these latter compounds were antithetic in their action, the one precipitating what the other dissolved. As reagents in the analysis of water, he employed extract of galls, syrup of violets, ammonia (for copper salts), and nitrate of silver, and showed that this last would detect one grain of salt in a thousand of water. His tables of specific gravities for different waters are the earliest on record.

Boyle differentiates between mechanical mixtures and chemical compounds. As a difference between mere mechanical mixtures and chemical compounds Boyle pointed out the homogeneousness of the latter in their minutest particles; he was aware, too, that no separation of their components was caused by the action of gravity. Though he knew that the different compounds of one element resembled neither their components nor one another, he saw that they often possessed some common features, as the blue colour of copper salts.

Calcination. John Mayow, 1645-1679. The increase in weight on calcining had convinced Boyle that something was absorbed rather than emitted during the operation, and yet he still regarded sulphur as a compound of its acid with some igneous principle; his conception of the atmosphere as a medium made up of particles terrestrial and astral, besides others permanently elastic, was not more satisfying.

A treatise appeared in 1674, written by John Mayow, in which these matters were thoroughly investigated. Mayow, by means of sulphuric acid, had precipitated sulphur from a compound of sulphur and potashes—the long-known “Hepar Sulphuris.” This fact, as Mayow at once saw, was entirely incompatible with an acceptance of sulphuric acid as a constituent of sulphur, for, were Boyle’s theory correct, the presence of sulphuric acid should rather tend to protect than destroy “Hepar Sulphuris.” Now Mayow, like Boyle, conceived the air as made up of minute particles, while he restricted himself to two varieties, those, namely, which are necessary to life, called by him “spiritus igno-aereus,” and those incapable of supporting respiration or combustion, which are left after the removal of this “spiritus.” Since a mixture of saltpetre and sulphur continued burning even under water, he assumed that his igno-aereal particles must also be contained in the salt. Acids, too, contained the new principle. The calx of antimony obtained by treating the metal with nitric acid was identical with that left after heating antimony in air. Sulphuric acid might be obtained indifferently by burning sulphur in air or boiling with aqua fortis, and must therefore contain something common to both media. Iron pyrites also would absorb the “spiritus igno-aereus” on exposure, for the green vitriol which resulted yielded sulphuric acid on distillation. Mayow died in 1679 at the age of thirty-four years; had he lived but a little longer, it can scarcely be doubted that he would have forestalled the revolutionary work of Lavoisier, and stifled the theory of phlogiston at its birth. As it was, his work, though rendered in one of the most luminous and convincing scientific publications of the period, was immediately forgotten, and so proved of little effect on the evolution of our modern chemical system.

Mayow's
“spiritus
igno-
aereus.”

The continental chemists contemporary with Boyle and Mayow were of an entirely different mental calibre. The German Kunckel was essentially an experimentalist; he was imbued with a belief in the philosopher’s stone, and regarded mercury as the necessary component of a metal. Kunckel was

Kunckel,
1630-
1702.

born in 1630, and died in 1702. He was the son of an alchemist, and himself passed much of his life as the employé of sundry German princes in the unsuccessful pursuit of the philosopher's stone.

Kunckel reduces blow-pipe. Before the second half of the seventeenth century the blow-pipe had been used neither in chemical analysis nor for working glass. It was Kunckel's task to demonstrate the ease with which a metallic calx might be reduced by heating it on charcoal before the blowpipe, and to institute a more expeditious mode of hermetic sealing than that of inserting the drawn-out neck of flask or other vessel in a hot fire, hitherto in vogue.

Kunckel was the first to recognize an analogy between putrefaction and fermentation and to show how the production of vinegar in the latter process depended on the initial formation of alcohol and avoidance of low temperature or presence of acids. With Boyle he may be regarded as an independent discoverer of phosphorus. This element had already been prepared about the year 1674 by Brand of Hamburg by a process which had remained a profound secret. There had been talk, however, of urine being an important factor in the operation, and Kunckel, on heating this with sand, obtained its precious ingredient.

Lemery, 45-15; his *Cours de Chimie*. The great achievement of the Frenchman, Lemery was his *Cours de Chimie*, which appeared in 1675, and long remained the standard text-book on the subject. Lemery separated all substances into three main divisions, vegetable, animal, and mineral, classifying under these heads not only those bodies which obviously belonged thereto, but also the products of their distillation. Like Tachenius, he defined his sel salé (our salt) as a mixture of acid and alkali. Lemery was aware that a mixture of iron and sulphur when moistened became hot; and this fact led him to an explanation of volcanic phenomena. He also thought the lightning flash might be due to the combustion of large quantities of hydrogen, a gas which had been discovered by Paracelsus, though confused by him with air.

The work of Homberg is of interest as being the first in which the balance was definitely employed in the elucidation of chemical problems. It is significant that Boyle had found it necessary to point out that silver chloride, precipitated from silver solution, weighed more than the original metal. In 1699 Homberg, who had been working for some time in Boyle's laboratory, began an investigation of the strengths of different acids. His method was to treat them with alkaline solutions, evaporate the mixture to dryness, and weigh the salt that remained. He noticed that with the same quantity of potash this weight was always the same, whatever the acid, and hence concluded that the strengths of these acids were all equal, and only appeared different because of the different quantities of water diluting them.

Homberg,
1652-
1715.
Use of the
balance in
determin-
ing relative
affinities.

All general conceptions of acids and alkalis were still very much confused, to such an extent, indeed, that Kunckel regarded alkalis and acids as mutually convertible. Boyle, and after him Becher, believed in the existence of some one primordial acid, of which the common acids were merely impure forms. This acid, in Becher's opinion, approximated closely to hydrochloric. Sylvius had ascribed acidity to fire matter, Lemery to fine points, and Mayow, with some show of reason, to his "spiritus igno-aereus." By an alkali, on the other hand, was understood any substance which effervesced with acids, fixed and volatile alkalis being grouped together.

Confused
ideas about
acids and
alkalis.

Why there should be combination between acids and alkalis, or, indeed, between substances of any kind whatsoever, had till the time of Boyle almost escaped question. Boyle supposed the reason to lie in the mutual attraction of the smallest particles, an attraction different from that of gravity in that it decreased more rapidly with the distance. He explained accordingly the decomposition of cinnabar on heating with potashes,—“the parts of the alkali associate themselves more strictly with those of sulphur than these were before associated with those of mercury.” Becher, on the other hand, regarded combination as a magnetic phenomenon.

Combina-
tion of
acids with
alkalis.

The connotation of the word "salt" was indefinite. Originally the word had implied any substance which was soluble in water or possessed a marked taste. Acids and alkalis were accordingly found classed with ordinary rock salt, though some discrimination was suggested by the subdivisional titles, "salia acida," "salia alcinina," and "salia salsa" respectively. Knowing this, we are the less surprised by Kunckel's belief in the transmutability of acids into alkalis. When it was discovered, however, that substances produced by mixing acid and alkali, the "salia salsa," were neither acid nor caustic, a new term seemed necessary. Such substances were certainly of a different order to the "salia acida" and "salia alcinina," and might well receive the general appellation "salia neutra." The word neutralization was soon the common property of chemical literature. But many of these neutral salts contained no metallic components; they were earthy salts. To discriminate between such and those that did contain a metal, the latter were termed "vitriols," a term first suggested by Magnus as the suitable designation of the glassy ferrous sulphate. The later chemists, however, separated vitriols from salts, regarding as such only those substances with marked vitreous glance or of definite metallic origin. It was Lemery who first defined vitriols as minerals composed of an acid salt and sulphurous earth, classifying them, however, not as salts, but as half-metals.

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Questions as to the ultimate components of matter were yet more confusedly answered. Not even Boyle and Kunckel were convinced of the untenability of the alchemist's position. In speaking of sulphur, Boyle struck the keynote of the whole period; he regarded it as compounded of sulphuric acid and something, certainly an element, which he termed "fire matter." Here was Valentine's philosophy again, nor do we miss its influence in Kunckel's belief that mercury was an essential component of the metals. Neither Boyle nor Kunckel, however, was sufficiently hardy to see sulphur and mercury in all matter. Yet something approaching a whole-hearted if enlightened acceptance of Valentine's theory we do find in the German Becher's *Physica subterranea*, published in 1669.

This work marked a reaction, but its contents were sufficiently weighty to lead Stahl later to his doctrine of phlogiston. Becher believed all matter to be made up of four elements, water and three primitive earths, the vitreous, the mercurial, and the combustible. It was this combustible earth, this "terra pinguis," whose expulsion from compounds caused all the phenomena of combustion.

The ancients had considered the calcination of metals and the burning of wood—processes which they believed to be identical—as the direct result of the separation of their element fire, and from the greater or less inflammability of a substance had argued its greater or less content of this fire. The Arabs, and Western nations, on the other hand, compared the calcination of metals to the burning of chalk, and hence gave to our literature the words "calx" and "calcination." Geber, and subsequently Magnus and Paracelsus, adopted in principle the ancient view, though for fire they substituted their element sulphur. Becher's "terra pinguis" had much in common with the fire of the schoolmen and the sulphur of Geber. This sulphur, as we have seen, was by no means identical with the common substance of that name, which, indeed, as Boyle had demonstrated, itself burnt with the production of an acid body. Years before Sylvius had spoken of an oily principle being so eliminated. Sylvius's oily principle and Becher's "terra pinguis" germinated in the brain of Stahl, whence there now issued the first comprehensive theory of combustion, the theory of phlogiston.

Stahl had early become convinced of the soundness of Becher's theory of the "terra pinguis," and had given utterance to his conviction. It was in his *Specimen Becherianum*, which appeared in 1702, that he pronounced himself most clearly. He maintained that all the phenomena of combustion were associated with evolution of phlogiston, an element which was an essential component of all combustible matter. Metals and sulphur, then, were compound bodies and the products of their combustion elements. Every phenomenon,

Philosophy of combustion prior to Stahl.

Stahl, 1666-1734; his theory of phlogiston.

in fact, which is now explained as being the result of a combination with oxygen, was with Stahl due to the escape of phlogiston. What this phlogiston might be Stahl did not precisely declare, but that it formed the chief component of soot seemed evident, for metallic calces, on being heated with this soot, regained their original metallic form, and sulphuric acid was converted into sulphur. Nothing but the soot could have restored the necessary phlogiston. Sulphur would not combine with metallic calces, and was therefore certainly not itself the necessary element of fire. It was only at the moment of combustion that the phlogiston became obvious to the senses. Prior to this it had remained hidden in the combustible substance—a deduction less happy, in that Van Helmont and Newton had both denied the corporeal existence of fire, believing it to be merely an outward and visible sign of intensely heated gas. After combustion, in other words, after complete or partial expulsion of phlogiston, there remained a calx, the other component of the substance burnt. If metals were investigated, their calces were always ultimately found identical, though admixture with impurity might more or less hide their identity.

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ition
emis- We can now understand Stahl defining chemistry as the art of resolving substances into their components and building them up again from these, a definition which had little in common with any that might have been suggested a half-century previous.

culties
cept-
Stahl's One would imagine that the increase of weight on calcination must have proved an insuperable difficulty to the general acceptance of Stahl's theory. It was not so, however. True, as time passed, there was felt some need of reconciling this increase with loss of phlogiston, a need, however, amply satisfied by the assumption that phlogiston, unlike any other material substance, was repelled from the earth, and that in consequence a calx was the heavier the more phlogiston expelled. It was maintained by some, and this time in direct defiance of Boyle's experiments, that the specific gravity of the calx was greater, and therefore, too, its absolute mass. As years passed, the

chief rôle of phlogiston was ascribed to the most widely different substances; at one time to the colouring matter of Prussian blue, at another to the gas hydrogen. Hence chemical nomenclature, which in many respects remained unaltered, must be interpreted differently during the successive phases of the period. Not only was phlogiston supposed to be an essential element in combustion; its existence also accounted for colour and varying solubility in acids, and for the analogy between respiration and combustion.

Since the time of Geber it had been known that air was necessary to combustion, and both Rey and Mayow had arrived at a reasonable explanation of this fact. But their work had been completely ignored. Stahl, following Becher, regarded the atmosphere as a purely passive agent in combustion, a suitable medium, and nothing more, for the reception of expelled phlogiston, and this belief long found general favour.

The part played by air in combustion.

Such, briefly stated, was that theory of combustion which has rendered the name of Stahl undying. Though exerting little influence on the work and preconceived ideas of his contemporaries, it became a guiding light to chemists of the succeeding generation. Speedily accepted in Germany and England, it made less progress in France till a translation of Juncker's *Conspectus Chemiae*, published in 1730, caused it to be generally received there also. As a practical chemist Stahl was prominent. His conceptions of the workings of affinity, based on laboratory work, were in advance of his time, his writings on fermentation those of a pioneer.

Reception of the phlogiston theory. Other work of Stahl.

The fermentation of plant juices and leavening of dough had as yet received no kind of serious explanation. As fermentations alchemists had classed the most diverse reactions, thus likening the transmutation of a base metal to the leavening of dough. Valentine thought the alcohol in beer, produced by the action of yeast on barley liquor, pre-existent in the liquid, though only capable of identification after separation of the other constituents. Van Helmont also knew of the presence of spirits of wine in fermented liquids, and sharply discriminated,

Fermentation

between it and the gas evolved during fermentation. Sylvius and Lemery took a step forward in looking upon ordinary effervescence as a result of combination, fermentation, on the other hand, as an accompaniment of decomposition. Lemery thought this type of decomposition due to an escape of saline particles (the carbonic acid gas), which separated the must into those grosser and finer parts, the scum and lees, with elimination of alcohol. A further advance lay in Becher's insistence on an analogy between fermentation, whether vinous or acetic, and combustion, Mayow having before this laid stress on the necessary presence of air at the initiation of both. Becher discovered that alcoholic fermentation only occurred in saccharine liquids, and even then only under suitable conditions; on addition of tartrate or alcohol the process stopped.

In 1659 appeared the *Diatribes de Fermentation* of the English chemist Willis. Its author maintained that fermentation was a decomposition brought about by communication of a vibratory motion to the particles of must, and the consequent shaking apart of their loosely combined components. These components could now enter into new combinations, of which one was alcohol. It was this theory which, forty years later, Stahl developed and spread abroad by his writings. Stahl took it that some watery fluid must be present to induce fermentation, or it might be putrefaction—they were analogous processes—which so influenced the unstable compound of salt, oil, and earth, that its constituents, fallen apart, had opportunity to reappear in new and more stable combinations. By the vinous fermentation there was eliminated a substance in which a combustible part predominated; by the acetic this spirit took to itself excess of acid. This philosophy of Stahl's enjoyed a widespread reputation during the whole of the phlogistic period, and later was resuscitated by Justus von Liebig.

Stahl could not entirely escape his preconceived ideas; he could yet speak of the earthy and mercurial components, of metallic calces, of the primitive acid; and for the greater part of his life he believed in the possibility of transmutation.

Stahl's two most famous contemporaries were Friedrich Hoffmann, Hoffmann and Hermann Boerhaave; the former was born at 1660- Halle in 1660, and the latter shortly after at Leyden. Both 1742. were successful as medical practitioners. At that time no Boerhaave, provision was made for an exclusive pursuit of pure science. 1668-1738.

Hoffman did not accept Stahl's doctrines in their entirety; Hoff- the production of sulphuric acid on burning sulphur convinced mann's him that this latter was compound, while the reduction of "sal- metallic calces appeared only reconcilable with the assumption acidum." of a hypothetical "sal acidum," something akin to sulphuric acid, which, combining with the metal, formed a calx. Hoffmann's attitude was not, however, maintained by any attempt at practical verification, and was, moreover, devoid of the unifying intent of Stahl.

Magnesia as a peculiar earth had been hitherto unknown. Hoff- Hoffmann showed that those salts which gave an astringent taste mann's to many natural waters, and which had hitherto been classed practical under the generic term "nitre," were, in fact, quite different from researches. this, since they gave no nitric acid on distillation with vitriol; neither were they of the same crystalline form. Among these salts there was one possessed in a marked degree of the astringent property, a compound of a chalk-like body and sulphuric acid—a chalk-like body differing, however, from ordinary chalk in that its vitriol was readily soluble in water. The base of alum, too, he showed to be quite different from ordinary chalk. This work has the greater interest in view of the general impression which at the time obtained that all calces were identical in composition, allowing for slight admixture with impurity. Again, Hoffmann noticed that the gas which escaped from many natural waters was of an acidic nature; he observed, too, that it was this gas, this "spiritum sulphureum," which was essential to the solution of iron in water, for after boiling such a water, and so removing the gas, every trace of iron was precipitated.

Hermann Boerhaave, though contemporary with Stahl, Boer- scarcely mentions the theory of phlogiston; he himself allowed haave's that sulphur was compounded of sulphuric acid and a "pabulum" "ignis" "of

belief in
alchemy.

combustible oil (a "pabulum ignis"), but, with Hoffmann, regarded calcination as associated with the absorption of certain material particles from the air. Boyle had supposed that the increase of weight on calcining a metal might be due to absorption of fire-particles, but Boerhaave showed that a metal might be exposed to the strongest heat without its mass altering. Boerhaave retained a belief in alchemy, though his experiments did much to dissuade others. The extraordinary perseverance of the man is appreciated when one learns that he preserved mercury for fifteen years at a slightly elevated temperature, in order to ascertain whether such an operation would cause any change in the metal, as had been maintained. He also distilled one specimen of the same metal five hundred times, that he might accentuate and observe that change in volatility, if such there were, quoted by the ancients.

Boer-
haave's
conception
of affinity.

The modern connotation of the word "affinity" was first given it by Boerhaave. Up to the end of the seventeenth century similarity in character had been regarded as indispensable to the combination of two bodies. Boerhaave maintained the direct contrary, and spoke of an *affinity* existing between solvent and solvend, between acid and metal, which caused their union. The idea seemed good, and the name became general, though endeavours were made later to replace it by some less specific term.

gradual
develop-
ment of
the idea of
multiple
elective
affinity.

The exceeding vagueness of all general ideas of chemical composition and of the nature of chemical action had necessarily precluded any attempt at ascertaining the relative affinities of different substances for any one definite reagent, and it is not therefore surprising that no explanation of any case of simple elective affinity was offered before the middle of the seventeenth century. In 1648 Glauber suggested that the expulsion of ammonia from its salts by chalk or potashes might be due to the superior attraction of the latter for the acid of the ammonium salt; and Sylvius, in 1659, gave a similar explanation of the precipitation of copper from its solutions by another metal. This idea, that different substances possess affinities of different

strengths for some third substance with which they can both combine, gradually became familiar. Glauber had already arranged gold, silver, copper, and iron in the order of their affinities for mercury, and later Boyle pointed out that while copper precipitated silver from its solutions, it was itself displaced by zinc or iron, facts which, together with the precipitation of solutions in acids by alkalis, and of sulphur from "Hepar sulphuris," he explained entirely in the spirit of Glauber and Sylvius. Later, Homberg had found the strength of all acids, as judged by their behaviour with potash, equal. In attacking the question of relative affinities, Stahl made use of the simple process of heating one metal with the sulphide of another, and observing with which the sulphur remained combined, and was thus able to arrange the various metals in the order of their affinities for this element. Reasoning similarly from the results of treating the salt of an alkali with acid, he concluded that sulphuric acid was a stronger acid than nitric, and nitric than hydrochloric.

In 1718 there appeared a paper in the memoirs of the Paris Academy, containing sixteen tables of affinity. This paper was written by Stephen Franz Geoffroy, a native of Paris, born in 1672. In drawing up these tables he adopted the system of arranging various acids and alkalis in two columns, headed respectively by an acid and alkali; and this in such a way that any alkali was displaced from its compound with the common acid by treatment with any other above it in the series. In obtaining the necessary data for the drawing-up of this table, Geoffroy worked on the assumption that if any two bodies with a tendency to combine were brought together, and there intervened a third, having more affinity for the one than the other, combination would take place in such a way that the strongest affinities were satisfied. And so he found himself able to compare the relative affinities of various metals and bases for the several acids, and of these acids for the metals. These *Tables des Rapports* of Geoffroy soon became popular, and gave rise to much experimental work, by which they were later enlarged and improved. The real nature of affinity, however,

Geoffroy,
1672-
1731. His
*Tables des
Rapports.*

still remained a matter of vague speculation, and the supposition of Boyle, that affinity was something analogous to, though not identical with, gravity, retained its popularity.

Geoffroy's
views on
combustion.

Geoffroy's views on combustion were in principle those of Stahl, though he expressed himself in the nomenclature of the earlier period; yet there was much promise in his conviction that the different calces were radically different bodies.

Neumann,
Eller, and
Pott.

Among the generation of chemists succeeding Stahl, Germany produced few of any note. Neumann, Eller, and Pott were active propagandists of Stahl's doctrines, and did much to keep chemical science to the fore in their country. Certain notable achievements, too, are associated with their names; the first accurate observation of the acid obtained from ants with that of Neumann, the solution of a salt in the saturated solution of another with that of Eller, and a wide extension of the method of dry analysis with that of Pott.

Marggraf,
1709-
1782. He
discovers
sugar in
roots.

Neumann's pupil, Marggraf, was the last of the well-known German chemists of the phlogiston period. Andreas Sigismund Marggraf was born at Berlin in 1709, and proved a most able experimenter; indeed, it is for his many isolated discoveries that he is remembered rather than for any influence exerted on the general trend of chemical philosophy. One of the most lasting benefits which we owe him was the introduction of the microscope as an aid in laboratory work. The occasion was noteworthy. A paper appeared in the memoirs of the Berlin Academy for 1745, in which Marggraf stated that small crystals of sugar might be seen with the aid of a microscope upon the finely divided and desiccated roots of the carrot and beetroot. He further stated that this sugar could be extracted by lixiviation with hot alcohol, and added that mere compression of carrot or beet would yield a saccharine liquid, from which the sugar might readily be extracted. These observations remained unnoticed, until the continental blockade of France in 1806 urged its people to find some substitute for their imported sugar.

Marggraf's

Of prime importance was Marggraf's discovery of phosphoric

acid, whose principal physical and chemical properties he accurately described. He obtained this acid by burning ordinary phosphorus in the air, and dissolving the resulting "fleurs de phosphore" in water; also by heating phosphorus with concentrated nitric acid. In view of these results, phosphorus could only be regarded as a compound of the acid so obtained with phlogiston. Marggraf's work on the composition of gypsum was remarkable; he had noticed that potassium sulphate on heating with charcoal emitted the pungent smell of burning sulphur, and as this also occurred when gypsum or heavy spar was substituted for the potassium salt, they too must be compounds of sulphuric acid. One should not forget his introduction of potassium ferrocyanide as a reagent for iron, nor his separation of microcosmic salt from urine; he remarked that it was this salt which contained the phosphorus.

contributions to pure chemistry.

Contemporary with Marggraf was Duhamel du Monceau, a native of Paris. Duhamel's great achievement was the differentiation of the two alkalis, soda and potash. The composition of ordinary salt had hitherto eluded research. Stahl, it is true, believed one constituent to be an alkali, and an alkali quite different from potash, if one might judge by differences in the crystalline form and solubilities of their respective salts. There was a vagueness about his work, however, and it had met with little recognition. Duhamel published a paper in 1736 on sea salt, which put the matter beyond question. In it he first showed that the base of salt was not an earth, for the addition of potash caused no precipitation, then that its several salts all differed essentially from those of potash corresponding. He laid stress, too, on the fact that the further one moves from the sea, the less the quantity of the new base and the greater the quantity of potash in the surrounding vegetation. Subsequently, while describing minutely the differences between the analogous salts of these bases, Duhamel mentioned the yellow and violet colorations which they respectively give to a colourless flame.

Duhamel du Monceau, 1700-1781: the differentiation of potash and soda.

To another Frenchman, Baron, we owe the clearing up of the mystery which had hitherto surrounded the composition

Baron, 1715-1768. The

composition of borax.

of borax. The name borax, or rather "baurach," had been employed by the Arabians indifferently in speaking of the true borax and nitre; its nature had served them as the goal of many fruitless investigations. Homberg had discovered boric acid (his sedative salt) in 1702, obtaining it by acting on borax with sulphuric acid, and Pott, in 1741, had shown that ordinary Glauber's salt was produced at the same time; but the conclusion that borax is a compound of boric acid and soda was Baron's.

Rouelle, 1703-1770; his definition of a salt.

Homberg's term for boric acid, "sel sédatif," had become superannuated, for Rouelle, a demonstrator of chemistry in the Jardin du Roi, had defined salts once and for all time as compounds of acids with base. He had separated them into three classes, discriminating between those with excess of acid, those with excess of base and neutral salts respectively; and had, moreover, shown that this excess of acid or base was not merely mixed, but combined. Rouelle it was who taught the concentrating of nitric acid by distillation with sulphuric acid.

Macquer, 1718-1784; his views on phlogiston.

Yet another French chemist, Macquer, adorned the period now at its fall. Macquer, born in 1718 and dying in 1784, saw the phlogiston theory attacked in its strongholds, without, however, losing faith. His phlogistic bias lent peculiar interest to his work on Berlin blue. He had heated this substance, and so discharged its blue colour, discharged it too by boiling with potash, and had argued that the colouring matter must therefore be pure phlogiston, that Berlin blue must contain an acid soluble in potash, and finally that this acid with phlogiston and alkali were the components of the salt he called phlogisticated alkali (our potassium ferrocyanide). Macquer introduced the method of separating salts by means of alcohol. He was the first to isolate the potassium salt of arsenic acid, which he obtained by heating white arsenic with nitre; he was able also to prepare the analogous salts of sodium and ammonium.

The English School of Chemistry

Since the time of Boyle no English chemist had produced any work of first importance. But now with the second half of the eighteenth century came Black, Priestley, and Cavendish,

men whose epoch-marking work was to make the name of England honoured throughout the whole scientific world. With them chemistry at once entered on a new phase. The exact quantitative spirit of Black and Cavendish and the pioneering genius of Priestley found powerful collaboration in the work of the Swedes Bergman and Scheele. By the united efforts of all, the foundations of the phlogistic philosophy were so effectually sapped, that small effort allowed Lavoisier to demolish its whole superstructure and substitute his all-sufficing oxygen theory.

Joseph Black was born in 1728; he was of Scotch parentage, and subsequently became professor of chemistry in Edinburgh. He began his scientific career a convinced phlogistonist, but in his latter days was a convert to the Lavoisierian school. Black's most memorable achievement was his discovery of the composition of the mild and caustic alkalis. It had been long known that limestone becomes caustic on heating, and in consequence causticity had been conceived as resulting from absorption of fire-particles. But on boiling this caustic lime with potashes, these in their turn became caustic, with the simultaneous regeneration of the original limestone. The mild alkalis (our carbonates of potash and soda) were therefore regarded as elements, and the transference of causticity from lime to potash as a mere transference of fire matter or phlogiston. Now Duhamel, in 1747, had shown that ignition of limestone caused loss rather than gain in weight, a loss which, however, was made good on exposure to the air; but here he had stopped. The publication in 1755 of Black's paper concerning some experiments on magnesia alba and chalk spread light over the whole question. Black found that magnesia alba and chalk both, indeed, lost weight on ignition, a loss due to the expulsion of a gas called by him "fixed air"; also that magnesia and chalk, after ignition, saturated the same quantity of acid as before, but that they now dissolved without effervescence; again, that the addition of potashes to the solution of lime or magnesia so obtained caused precipitation of a substance equal in weight and identical in properties with

Black,
1728-
1799; his
researches
on the
mild and
caustic
alkalis and
recogni-
tion of
"fixed
air."

the mineral originally taken, the potash at the same time becoming caustic; and finally that caustic lime could be rendered mild by treatment with magnesia alba, though not if the latter had been previously ignited. The enigma was solved. When lime became caustic, something was lost, and this something was the gas evolved on solution in acids. The rendering caustic of potashes was similarly due to abstraction of a gas combined in them by the burnt lime. It was not surprising, therefore, that potashes like lime effervesced with acids, yet when rendered caustic were capable neither of this nor of precipitating lime-water. The scum found on lime-water that had been exposed to the atmosphere found a ready explanation, also the evolution of ammonia on boiling its carbonate with caustic potash. Black was the first to insist on the fact that a gas can enter into chemical combination. He may be regarded as the discoverer of carbonic acid gas, his "fixed air," which he showed to be no other than choke damp.

Meyer's
theory of
causticity,
1764.

Black's paper seemed conclusive, yet his views were long in gaining universal acceptance. Appreciated at their just worth in England, they met with much opposition in Germany, notably from one Friedrich Meyer, who, in a paper published in 1764, offered another explanation of the above facts, the chief merit of which was its entire accordance with the theory of phlogiston. Black's hypothesis offered no explanation of the heating which occurred on moistening burnt chalk with water. Now, Meyer maintained that while water, and water only, escaped on heating chalk, something was taken up from the fire, a something which he termed "acidum pingue." It was the partial expulsion of this from the burnt lime that caused a rise of temperature on addition of water. On mixing mild potashes with burnt lime, this acid principle was transferred to the former, and with it the causticity; and the alkali so obtained did not effervesce with acid, for the same reason that potassium acetate or sulphate did not; it was already saturated. It is interesting that Lavoisier, while speaking but coldly of the merits of Black's work, hailed Meyer's paper as a masterpiece.

Carbonic acid was the first gas to be definitely recognized as differing from ordinary air, and the field of pneumatic chemistry was practically virgin soil when Priestley and Scheele almost simultaneously set about its exploitation. Joseph Priestley was born in 1733, in the neighbourhood of Leeds. A Nonconformist minister by profession, he took up chemical research merely as a pastime, and one is therefore hardly surprised at a certain lack of method in his experimenting.

Priestley,
1733-
1804.

The method, first employed by Boyle and Mayow, of collecting gases over water was quite common when Priestley began his work. From this Priestley at times deviated in substituting mercury for water, and hence resulted the discovery of many gases—sulphur dioxide, ammonia, hydrochloric acid gas, and silicon tetrafluoride—whose solubility in water had hitherto prevented their isolation. Priestley's most famous discovery, however, was oxygen.

Priestley's
discovery
of many
gases
soluble in
water.

It is certain that oxygen must have been often prepared and collected before Priestley's experiment. Hales, some forty years before, had collected the gas, undoubtedly oxygen, given off on heating red lead; but being a gas its properties were of no interest to him, and he failed, therefore, to recognize its peculiar character. Priestley himself had obtained oxygen before by exposing minium to the electric spark, but had confused it with carbonic acid. Steeped as he was in phlogistic lore, he had considered the revivification of lead oxide by carbon and by the spark as entirely analogous processes, as both resulting in the restoration of the lost phlogiston, and hence, without further examination, had declared the gases evolved to be identical. A year after, in August, 1774, by means of a burning glass he concentrated the solar rays on some red oxide of mercury, and obtained a gas which, to his amazement, sustained the flame of a candle with vastly increased brilliancy. At first he thought this might be the same nitrous air he had obtained two years before by the action of nitric acid on copper; but the fact that its powers of supporting combustion were not exhausted by the prolonged burning of a candle, and that it did not give brown fumes with air, persuaded him that

The dis-
covery of
oxygen,
1774.

here, indeed, was something new. It was not, however, till the March of 1775 that he became fully convinced of the importance of his discovery. Finding that his new gas underwent diminution in volume when mixed with nitrous air (our nitric oxide) over water, he tried its effect on a mouse, and found that it supported life even better than ordinary air. To this gas, so eminently suited for supporting combustion, so free from phlogiston in the parlance of the period, he gave the name "dephlogisticated air."

Priestley's
method of
analyzing
air.
Ruther-
ford's dis-
covery of
nitrogen.

The behaviour of a mixture of nitric oxide and ordinary air had suggested to Priestley a method of analyzing the atmosphere, which he had so discovered to be made up of two gases in the volume ratio of one to four. That part which disappeared he now declared to be identical with his "vital air"; the remainder had already, in 1772, formed the subject of an investigation by Black's pupil, Rutherford, who recognized its peculiar character, regarding it, however, as a product of the combination of air with phlogiston, a phlogisticated air. Priestley was also able to show that airs collected at different times, and under the most varying conditions, differed but little in composition—a fact he rightly explained by associating vegetable growth with an absorption of vitiated air (carbonic acid) and subsequent emission of pure or vital air.

Hydrogen
as phlogis-
ton.

Priestley's contemporary, Cavendish, had identified hydrogen as a peculiar gas, and Priestley henceforth regarded hydrogen as the long-sought phlogiston. This belief he based on the revivification of metallic calces when heated in this gas; and he made some, for the time, exceedingly accurate quantitative estimations of the amount of hydrogen (phlogiston) required for the conversion of a certain weight of calx into metal. His surprise was great to find the metal so obtained always lighter than the calx employed; he could only explain the fact by assuming a volatilization of some of the calx, or solution of part of the resulting metal in the mercury employed in his experiments. The water simultaneously produced he believed to have been pre-existent in the hydrogen or calx.

Priestley

While Priestley was performing his random experiments, as

he called them, and enriching chemical science with a wealth of new gases, a countryman of his was equally hard at work; and it would be hard to decide to which of the two, Priestley or Cavendish, posterity owes the greater debt. Priestley discovered, Cavendish investigated: the former restlessly turned his hand first to one substance, then to another; the latter concentrated his whole energy on one point, and did not leave it till it was comprehended in its entirety. To the random experiments of the one we owe our first knowledge of oxygen; to the scientific method of the other the discovery of the composition of water and nitric acid. Their outward circumstances were as diverse as their inner consciousness. Priestley was the son of a mechanic, Cavendish the grandson of a duke.

Cavendish was born at Nice in 1731, two years before Priestley; but, notwithstanding his brilliant circumstances, he lived the life of a recluse, devoting himself entirely to the furtherance of his beloved science. He died in 1810.

Cavendish's first paper, that on "factitious airs," appeared in 1766, and described an exhaustive investigation of the two gases, hydrogen and carbonic acid. He laid stress on their absolute individuality—a point of much importance at a time when the idea prevailed that almost all gaseous bodies were identical with ordinary air—and introduced the system of using their specific gravities as a characteristic mark. Like Priestley, he identified hydrogen with phlogiston, and in the gas evolved on heating a metal with concentrated vitriolic acid saw a compound of this phlogiston with the acid.

Cavendish next applied himself to investigate the causes of the decrease in volume on phlogisticating air, and he was thus brought to discover that copestone of the antiphlogistic doctrine, the composition of water. It was in 1781 that Cavendish repeated a crude experiment of one Warltire, exploding a mixture of his inflammable gas with ordinary air. He, like Warltire, noticed the formation of dew; but with what different consequences! Warltire had given this dew no particular attention. Cavendish, on the other hand, connected it with the loss of elasticity which some of the hydrogen and

one-fifth of the common air had suffered. He repeated the experiment on a much larger scale, and collected a considerable quantity of the liquid; he examined it and found, there could be no doubt, only pure water. He now tried substituting pure oxygen for the common air, and once again obtained water, but this time with complete loss of elasticity to the reacting gases. Though this experiment proves that Cavendish knew what component of the air was called into play in Warltire's experiment, he left the engineer Watt first specifically to state that water was composed of dephlogisticated and inflammable air, Watt being at the time engaged in experimenting on the supposed mutual convertibility of water and common air. Cavendish showed that the weight of water obtained was equal to that of the gases employed, but could not at first explain an occasional acid reaction which this water exhibited. It was the investigation of this acidity which occasioned the delay in publishing an account of his investigations—they were only published in January, 1784—a delay which led to the unfortunate water controversy. For meanwhile the French chemist, Lavoisier, had repeated Cavendish's experiments, instigated thereto by hints received from Cavendish's secretary, Blagden, and had seemed to arrogate to himself the honours due to the discoverer of the composition of water. For many years it was war between the admirers of Cavendish, Watt, and Lavoisier: posterity has deservedly given the crown to Cavendish.

The composition of nitric acid and phlogistication of air by the electric spark.

Cavendish's experiments to determine the cause of acidity in the water were masterly. He neutralized the water with potash, and so obtained a small quantity of nitre; he heated this with carbon, and obtained nitrogen; he again exploded a mixture of hydrogen and oxygen, this time with the addition of nitrogen, and found the acidity of the deposited water increased—a final proof that the acidity was caused by phlogistication of the nitrogen added; Cavendish now turned to the phlogistication of air by the electric spark; and here again he noticed a fixation of the gases, especially in presence of potash solution. Again it was nitric acid that the potash

absorbed. By suitable additions of oxygen he was able to cause the almost total disappearance of the gases ; but in every case a small bubble was left which defied fixation. This phenomenon remained without explanation until the discovery by Rayleigh and Ramsay, in 1894, of the hitherto unknown argon.

To Cavendish also we owe the first accurate analysis of air. Analysis of air.
He adopted the method of Priestley and demonstrated the constant composition of the atmosphere ; his values for the volume percentage of nitrogen and oxygen were 79.16 and 20.96 respectively, numbers differing but little from those accepted at the present time, 79.04 and 20.96. Cavendish remained, in name at least, a phlogistonist. He admitted, however, that phenomena might be explained equally well by using the nomenclature of the old or new system. Yet the results of his work could bear but one interpretation to the unprejudiced mind, and no chemist of the succeeding generation was found to defend the moribund notions, and still more moribund nomenclature, of the phlogistic period.

The crowning glory of Priestley's scientific life was the discovery of oxygen. It was a coincidence of a type not infrequent in the history of science, that the Swedish chemist, Scheele, made the same discovery, quite independently, and almost simultaneously. Carl Wilhelm Scheele was born at Stralsund, in North Germany, in 1742, and died at the comparatively early age of forty-four. His opportunities were small, but after mastering the contents of Kunckel's, Neumann's, and Stahl's text-books, he set to work to verify their contents practically, being enabled to do this by his position as assistant in an apothecary's shop. In this way he laid the foundations of an extraordinary skill in manipulation. Scheele, 1742-1786.

While Priestley discovered oxygen in the August of 1774, Scheele's laboratory notes would show that the latter had already, more than a year previously, obtained the same gas from mercuric oxide, nitre, and various other substances. This gas, which he identified with his fire air—that constituent of the Scheele's discovery of oxygen.

atmosphere which sustains combustion—he thought to be composed of a saline principle with water, containing little, if any, phlogiston. On calcining a metal in air, this water combined with its grosser part, the saline principle taking up the phlogiston, and this with production of light and heat, which gave the inactive component of the air increased levity. Phlogiston itself he sometimes confused with hydrogen, while at other times, as when he spoke of “phlogisticated nitric acid,” he appeared to regard it merely as the antithesis of fire air.

Discovery
of chlo-
rine,
manga-
nese, and
baryta.

Scheele's paper on manganese dioxide appeared in 1774, and gave information of three discoveries, those of the gas chlorine, the metal manganese, which, however, was not isolated, and the earth baryta. To chlorine Scheele gave the name “dephlogisticated muriatic acid,” for he was of opinion that its evolution was consequent on the extraction of phlogiston from muriatic acid by the manganese mineral. He examined its properties with great care, and discovered its power of bleaching organic colouring matter. Baryta was a common impurity of the manganese ore used by him; its solutions he used later for the detection of sulphuric acid. Other discoveries of Scheele were those of hydrochloric acid and ammonia,—these quite independently of Priestley—of molybdic acid and tungstic acid, of arsenic and prussic acids.

Scheele
and
organic
chemistry.

Before Scheele organic chemistry had been almost entirely neglected. Though the chemists of the iatro period based all their claims on a supposed knowledge of the working of the digestive system, their views had scarcely extended beyond general conceptions of acidity and alkalinity. Such organic compounds as were necessarily produced during customary laboratory processes had, indeed, excited some attention, but these were not many. The acid of vinegar, benzoic acid, succinic acid, and acetone, bodies easily isolated by sublimation or distillation, were known; while all other vegetable acids, which proclaimed their existence through the sense of taste, were taken as forms of acetic acid; and certainly the fact that their investigation usually resulted in the formation of this

Scheele introduced an entirely novel method of separating these organic acids; he first prepared their insoluble lead or calcium salts, and then precipitated the base with sulphuric acid. In this way he isolated, for the first time, tartaric, malic, citric, and gallic acids, and was able to identify the acid of sorrel with that produced by the action of nitric acid on sugar. All these acids he examined rigorously, and showed how they might be differentiated, and how detected in their parent plant. When to all this we add his discovery of a new acid (uric) in bladder-stones, of mucic acid, and of glycerine, obtained by boiling various oils with litharge, and when we remember all he did for pneumatic and mineral chemistry, it is difficult for us to conceive how one man could do so much with but indifferent means at his command, within the short space of sixteen years.

That which Scheele did for organic chemistry another Swede, Torbern Bergman, did for analytical chemistry, giving to the whole system of quantitative and qualitative analysis a sound foundation. Bergman's circumstances were very different from those of Scheele, and as professor of chemistry in the university of Upsala, he had at his disposal every requisite of scientific work. He died in 1784, at the age of forty-nine.

Bergman's system of wet analysis first took form during an investigation of natural waters; but he later made it embrace the examination of minerals in general, fusing such of these as were insoluble in hydrochloric acid with carbonate of potash. Bergman laid great stress on the analytical value of the blow-pipe, between whose inner and outer flame he discriminated; and he endeavoured to extend the use of such reagents as soda, borax, and microcosmic salt, substances whose value had long ago been demonstrated by the mineralogist Cronstedt. It is to Bergman's pupil Gahn that we owe the introduction of cobalt solution as a reagent, and the substitution of platinum wire for the gold or silver used hitherto. Up to this time, reduction to the metallic state had been regarded as a necessary precedent to the quantitative estimation of metals in combination. Bergman now introduced the revolutionary method of com-

Bergman,
1735-
1784.

Bergman's
system of
analysis.
He deter-
mines the
phlogiston
content of
metals.

bining them in stable salts of known composition, and from the weight of these calculating the metallic content. Bergman's analyses were not very accurate, yet they enjoyed the widest popularity; On the other hand, his German contemporary, Wenzel, found little consideration, though his method was similar, and his results more fortunate. Meanwhile, the number of chemists who applied themselves to the quantitative side of phenomena was steadily increasing, an indication of the straits to which the phlogiston theory had been reduced. Yet at this eleventh hour Bergman set to work to determine the relative quantities of phlogiston in metals. Believing that metals only dissolve after conversion into their calces, he ascertained those weights of various metals which precipitated the same weight of some other in solution, surrendering their phlogiston to its calx; these weights, to his mind, contained the same quantity of phlogiston.

Bergman's
affinity
tables.

It was almost sixty years since Geoffroy had published his *Tables des Rapports*, and during all this time no modification or addition to them had been suggested. Geoffroy had regarded the relative affinities of bodies when in solution as identical with those determined at high temperatures, and this although Stahl had already shown that phenomena were often reversed by change of temperature, instancing particularly the action of silver on calomel. Baumé, in 1773, proposed the drawing up of two separate tables to represent the relative affinities at low and high temperatures respectively; and this scheme was carried into effect by Bergman. His tables resembled the earlier ones of Geoffroy; he did not attempt any absolute quantitative measurements, though he believed that if such could be obtained, the course of any reaction would be calculable.

Bergman's
influence.

Bergman's influence was immense; he was the authority to whom all questions relating to analysis or the problems of affinity were referred. It is the scientific spirit which he infused into his contemporaries, rather than any striking discoveries or brilliant experimental demonstrations, that ensures him an honourable place among heroes of science.

CHAPTER III

FROM LAVOISIER TO THE ENUNCIATION OF THE ATOMIC THEORY BY DALTON

IN the preceding chapter we have seen, somewhat vaguely it is true, how far the progress of chemical knowledge during the seventeenth century was influenced by the theory of phlogiston. As might have been expected, Stahl's theory, though exerting a marked influence, was not sufficient to restrict general attention to the phenomena of combustion, and it was too elastic to lend any precise definition to the trend of general investigation. This elasticity was in itself a sign of the only partial adherence which it obtained from those best qualified to judge of its merits. There is a value in comparing the duration of the phlogistic theory with that of the preceding iatro-chemical doctrine, and of the still earlier belief in transmutation. We so find evidence of a slowly developing critical spirit, which, with an ever-increasing ardour for experiment, brought ever speedier downfall to philosophies insecurely based.

The phlogistic theory had done good work. Its explanation of facts was truly scientific, and if it did not directly inspire much practical investigation, it did co-ordinate knowledge of what would otherwise have remained mere isolated phenomena. It brought to chemists, too, a feeling of unity of aim, by suggesting one general theory of reaction among bodies, whatever their origin, mineral, vegetable, or animal. That the theory was consistent with itself is obvious, since every phenomenon which it explained as caused by expulsion of phlogiston is now regarded as due to absorption of oxygen.

Value
of the
phlogistic
theory.

"The state"
of general
chemical
knew-
ledge.

And what was the state of general chemical knowledge in the decade previous to the establishment of Lavoisier's doctrine? The stability of the elementary nature was accepted by all, and the indestructibility of matter felt by most. The methods of qualitative analysis were reasonably certain when applied to the investigation of mineral matter, and the quantitative side of phenomena had been ably dealt with by Cavendish and Bergman. The differentiation of gases had been taught by Black and Cavendish, and the wealth of discovery from Priestley's chance experiments had opened up the rich field of pneumatic chemistry. Scheele had ventured into the domain of organic chemistry, and found a general method of attacking the problem of vegetable acids. Physiological chemistry must also have received some consideration; otherwise one could hardly account for the sudden change of face undergone by the medical faculty on the introduction of the new doctrine, for the dire havoc wrought by disciples of Paracelsus had hitherto caused the medical faculty to look askance on any attempt at co-ordination between physiological fact and chemical theory. Moreover, the problems of affinity had not been left untouched, and the work of Geoffroy, Stahl, and Bergman was sufficient to show students the value, if at the same time the difficulty, of their solution. As to what affinity really is, they knew as much almost, as we do at present.

A rigorous
quantita-
tive
method
marks the
new epoch.

What was it, then, in the philosophy of Lavoisier which inspired the progress we have now to detail? The new theory of combustion has certainly proved correct, and bodies hitherto accepted as elements have been proved compound; yet there must needs have been something more to mark an epoch in the history of our science. And, indeed, it was in the submission to a rigorous, all-embracing quantitative method, depending on absolute conviction in the permanence of matter as the criterion of all hypotheses, that we find the truest rationale of the advance. The way of progress had been groped for long, the times were ripe for its discovery, and Lavoisier was their chosen agent. One must not, however,

forget how much Lavoisier owed to his predecessors. Wurtz, in his history of chemistry, speaks of it as a French science founded by Lavoisier. If the real science of chemistry consists in the investigation of material substances, with a view to discovering their constituent parts and the truths underlying their interaction, a very cursory glance at the life-work of Boyle, Black, Cavendish, Scheele, and Bergman will show how far Wurtz's patriotic bias was accountable for his statement.

Jean Antoine Lavoisier¹ was born in Paris in the year 1743. Lavoisier,
His precocious development was no doubt due in some 1743-
measure to the excellence of the early education which his 1794.
parents, with their considerable means, spared no pains in procuring him. He was elected a member of the Académie Française at the early age of twenty-five, and a "fermier-général" the year following. From this time onwards his position was brilliant, and his scientific knowledge ever being called into requisition by the State. Yet not only was Lavoisier eminent as a scientist, he had views on his country's domestic affairs which were equally those of a revolutionary and a philanthropist. As secretary to the Board of Agriculture, he endeavoured to introduce reforms to ameliorate the conditions of the working classes, and did much on his experimental farms to demonstrate the means of their success. We find him, too, occupied with schemes for the founding of savings-banks, workhouses, and insurance societies. All the while, however, he remained a "fermier-général," and in this capacity had again shown originality in attempting to stop many abuses; and it was as a "fermier-général" that he was condemned by the Revolutionary tribunal in 1794 on the charge of "conspiring against the French people, tending to favour by all possible means the success of the enemies of France, . . . of adding to tobacco water and other ingredients detrimental to the health of the citizens." His head was struck off. He had powerful friends in the tribunal, but they stirred not a finger

¹ Cf. Hoefer, *Histoire de la Chimie*, ii. pp. 489 et seq.; also Thorpe, *Essays in Historical Chemistry*, 1st ed., p. 87.

to save him. These friends, Fourcroy, Monge, Morveau, and Laplace, had named the new chemistry "French chemistry," and, with Lavoisier alive, there seemed little chance of its being dissociated from his name. Years before this, too, Lavoisier had criticized, with the severity of truth, Marat's essay on Fire, and Marat was now in power. In the year following the French nation awoke to the enormity of the crime that had been committed, and Lavoisier's remains were awarded a solemn funeral; his *éloge* was spoken by Fourcroy!

There are few great men who are not open to criticism; Lavoisier has a name which will be revered to all time by the posterity of all nations; already during his lifetime his scientific pre-eminence was recognized throughout Europe. Yet he was not content. The desire of fame is one of the elements of human progress, and its consummation the deserved reward of the philosopher. Priestley and Cavendish are among the immortals; they discovered oxygen and the composition of water. Lavoisier's¹ eye was envious, and he would have claimed these discoveries for his own.

Lavoisier's
theory of
combustion.

It is probable that Lavoisier's mind was turned towards the consideration of the air and the phenomena of combustion so early as 1770. The three questions which seem to have arrested his attention were those of the composition of air, of the increase in weight of elements on calcination, and perhaps of the sufficiency of the phlogistic theory; for in 1772 he found it necessary to admit that "*even yet* we do not know enough of phlogiston to say anything precise about it." And very true this was, for among the phlogistonists there was unanimity only when the existence of phlogiston itself was called into question. What it might in reality be, no two chemists were agreed. One thought it elementary, another compound. Perhaps it was the material part of light; perhaps, on the other hand, far from being material, it was the principle of levity itself. The reader may remember that Mayow had expressed views on the nature of combustion

¹ Cf. Thorpe, *Essays in Historical Chemistry*, 1st ed., pp. 110 *et seq.*; Kopp, *Geschichte der Chemie*, i. p. 306.

closely in accord with what we know now to be truth ; other chemists, too, had made observations on the same matter far in advance of their times, and consequently barren. It may be that Lavoisier was incited to his fruitful labours by his study of these bygone philosophers ; it may be the spur came from within. Certain it is, however, that in 1772 he found combustion of sulphur or phosphorus in air brought increase in weight, just as had been found to happen with metals, and this with simultaneous absorption of air. A metallic calx heated with carbon gave off a gas which Lavoisier supposed had been taken from the atmosphere, an error which is readily understood and condoned, when one remembers that carbonic acid contains its own volume of oxygen. He soon convinced himself, however, that this gas really contained carbon united to part of the calx, yet in rectifying this error he fell into another, believing that the province of the carbon used was merely to give back phlogiston to the air fixed in the calx.

And now a small but instructive point.¹ Lavoisier knew that carbonic acid gas, like that left after the combustion of phosphorus, would not support the flame of a candle, and so he differentiated them, curiously enough, by their effect on animals. These, he said, will live in the after fumes of phosphorus, while they are instantly killed by carbonic acid, the correctness of which statement was solemnly affirmed after experiment by Macquer and other credible witnesses.

In 1774 Lavoisier performed an experiment on the calcination of tin,² which has become classic. He heated tin in a closed flask, weighing the whole before and after ; there was no increase in weight, so, clearly, heat was not ponderable. The flask was then opened, air rushed in, the whole was weighed again, and there was found an increase, an increase almost equal to that in the weight of the tin. But Lavoisier had shown already that the air left after calcination of a metal was incapable of supporting the combustion of a candle ; he could now, therefore, state explicitly that the increase in weight

¹ Hoefer, *Histoire de la Chimie*, ii, p. 501.

² *Ibid.*, p. 502. —

of his tin was solely due to the absorption of some of the air in which its calcination had occurred; that atmospheric air was made up of two gases, salubrious and non-salubrious; and, incidentally, that the most salubrious portion of the air, which he believed to be that absorbed, was specifically heavier, and the azote left specifically lighter than ordinary air. His theory of combustion was thus nearly complete; there remained only the isolation of the most salubrious ingredient, and in the October of 1774, Priestley, visiting Paris, was able to tell him of his own great discovery in the preceding August. Lavoisier at once grasped its full meaning, and set about its experimental verification. Compare the following experiment with that of the brilliant amateur, Priestley. Some mercury was heated in a retort, and the diminution in volume of the contained air measured; the grains of red oxide were collected, weighed, and again heated, and the gas evolved measured.

As Priestley had told him, this gas proved eminently suited for sustaining a flame and respiration. A few more experiments on the combustion of diamond in air and in the new gas of Priestley convinced Lavoisier of the true meaning of revivification of calces by carbon. The carbon combined with that gas whose absorption from the air had caused all the phenomena of calcination and combustion.

Oxygen,
the cause
of acidity;
its com-
pound
with
hydrogen.

Observation of the combustion products of phosphorus, sulphur, and carbon told Lavoisier that acidity was certainly to be associated with an absorption of dephlogisticated air. In a paper¹ "On the nature of acids," read before the Academy in 1778, he remarks, "I shall henceforth designate it," the dephlogisticated air, or the eminently respirable air, "by the name of the acidifying principle, or if it be preferred to have the same signification under a Greek word, by that of the principle oxygen." And Lavoisier naturally thought that the body produced by burning hydrogen in this oxygen would be an acid, and was therefore prejudiced when estimating the results of numerous experiments he had made on it. Finally, however, in 1782, he received information from Blagden of

¹ Cf. Kopp, *Geschichte der Chemie*, iii. p. 212.

Cavendish's work, and, after repeating it, found his explanation of the whole of the phenomena of combustion completely verified. His mental grasp is here shown very clearly; if, he said, water can be made by the union of hydrogen with oxygen, then, after taking away this oxygen, hydrogen should remain; a fact which he then verified experimentally by passing water vapour over iron filings heated in a gun-barrel. So the production of water by the action of hydrogen on metallic calces was no longer a mystery, nor the evolution of hydrogen on dissolving metals in acids. It was the physicist, La Place,¹ who first took this hydrogen as coming from the water, whose oxygen, combining with the metal, formed its calx, which dissolved.

All these years Lavoisier² had been fighting the scientific world single-handed; until the composition of water was discovered, and its bearing on the questions at issue recognized, even the French school held aloof from the radical change he advocated. But we now find Fourcroy, Berthollet, and Monge giving their allegiance with enthusiasm to his "pneumatic theory," as Fourcroy called it. In England opposition was continued till, finally, in 1791, even Kirwan,³ the last doughty opponent of reform, and one who, regarding hydrogen as phlogiston, had carried on a long and skilful controversy with the French savants, laid down his arms, admitting himself overcome by the overwhelming proofs that Lavoisier had brought forward. Germany, the birthplace of the phlogistic theory, was most refractory; her political relations with France may have contributed something to this, for only with the close of the century did she offer the new philosophy welcome.

Spread of
the anti-
phlogistic
doctrine.

The whole science of chemistry seemed to centre now in oxygen. It was oxygen which supported combustion, oxygen which conferred acidity, hydrogen which the medical faculty seized on as the "deus ex machina" to solve all problems of

The rôle
of oxygen
in chemis-
try.

¹ Hoefcr, *Histoire de la Chimie*, ii. p. 522.

² Cf. Kopp, *Geschichte der Chemie*, i. pp. 317, 341.

³ Cf. *Essai sur le Phlogistique et sur la Constitution des Acides*, traduit de l'Anglois de M. Kirwan. Paris, 1788.

pathology. At one time disease was traced to excess of oxygen, and carbonic acid prescribed; at another, if the symptoms suggested deficiency of oxygen, acids and oxygenous bodies generally were taken as antidotes. It is true that many prominent physicians and chemists protested against these extravagances, though perhaps the discovery of galvanism, with the new and more elastic basis for theorizing it supplied, was their most effective enemy. Such aberrations are always found when men have become suddenly aware of some all-pervading truth; and, indeed, it is a leaning towards fanaticism that supplies the motive-power for overcoming time-honoured superstitions.

Lavoisier
and
organic
chemistry.

Inspired by his new doctrine, Lavoisier now applied himself to investigate the combustion of organic bodies in air. Finding carbonic acid and water invariably produced, he could postulate the presence in them of carbon and hydrogen certainly, and he soon found, moreover, that many substances, markedly those of animal origin, contained sulphur, phosphorus, and nitrogen in addition. He determined the approximate quantitative composition of several organic bodies by heating a known weight of the substance with a known weight of red mercury oxide, and weighing the carbonic acid and water produced. He knew the oxygen content of the mercuric oxide, and so could discover how far this supplied the carbon and hydrogen with the oxygen they needed, and how far this was furnished by the compound under investigation. Lavoisier in this way determined the composition of alcohol, and how he used this in further experiment may be judged by the following:—3¹ oz. 7 gros of water were mixed with 2 lb. 8 oz. of sugar, and after fermentation there was left 1 lb. 7 oz. 5 gros 18 gr. of alcohol, 1 lb. of carbonic acid having been evolved. The 2 lb. 8 oz. of sugar might then be taken as composed of 1 lb. 8 oz. of alcohol and 1 lb. of carbonic acid, or, in terms of the elements composing them, of—

¹ 72 grs. = 1 gros. (Cf. Hoefer, *Histoire de la Chimie*, ii. p. 526.)

8 gros = 1 oz.

16 ozs. = 1 lb.

			lb.	oz.	gros	grains	
Hydrogen	0	3	4	49	} alcohol.
Oxygen	0	8	0	54	
Carbon	0	12	2	41	

and—

Oxygen	0	11	4	12	} carbonic acid.
Carbon	0	4	3	60	

If we add the values for carbon and oxygen, we obtain a composition for sugar, which may be compared with that accepted nowadays.

			LAVOISIER.					MODERN VALUES.			
			lb.	oz.	gros	grains		lb.	oz.	gros	grains
Carbon	1	0	6	29	...	1.	0	6	23
Oxygen	1	3	4	66	...	1	4	4	48
Hydrogen	0	3	4	49	...	0	2	4	43

But the whole system of quantitative organic chemistry was too young for Lavoisier to foresee the nicety with which Liebig, later, could handle these methods of ultimate analysis; he regarded his experiments as merely confirmatory of his system, the composition of sugar a mere incident. Organic bodies in general he took to be oxides of a radical, which might itself contain hydrogen and carbon, or in some cases these together with nitrogen, sulphur, and phosphorus.

Lavoisier's analyses of inorganic, as of organic bodies, were based on cogent reason. Here, again, he reduced chemical phenomena to equations, ever insisting that the weight of a compound is equal to the aggregate weight of its component parts. To take a specific instance, that of nitre; the action of sulphuric acid on this salt was expressible thus, where x and y stand for its basic and acid radicals respectively: $x + y +$ vitriolic acid produce nitric acid and potassium sulphate (tartre vitriolé); whence it was obvious that nitre must be the nitric acid salt of potash.

The evidence was strong in favour of Lavoisier's contention that it was oxygen that conferred the property of acidity;¹ with scarcely an exception the oxides of the non-metallic elements

Inorganic analysis.

Nomenclature.

¹ Kopp, *Geschichte der Chemie*, i. pp. 108, 109.

were acids. An experiment which Lavoisier performed with the mercury salt of vitriolic acid added curiously to the strength of his conviction. On heating this salt it broke down into oxygen and the common oxide of sulphur; vitriolic acid was then a higher oxidation product of this oxide, its acidic properties being certainly more marked. That oxidation did sometimes occur by such distinct steps had been observed, too, in the case of other elements, metallic and non-metallic, whence it followed that confusion in the mention of these oxides was hardly to be avoided. This and the existing trend towards quantitative exactness inspired Lavoisier, Morveau, Berthollet, and Fourcroy, in the April of 1787, to lay a new system of nomenclature before the French Academy. Already, in 1782, Bergman¹ had taken steps in the right direction by suggesting that each acid should be given some simple name, which should be given also to all its salts, that of their bases being added to mark the species. He had suggested "nitreum" and "nitrosium" for our nitrous and nitric acids. Bergman had not been, however, himself consistent in the use of his terms. Morveau had gone beyond Bergman, but not much; he was still a phlogistonist. Yet it was an advance to have the name of a salt combining those of its mother acid and base, the salts of vitriolic acid being called vitriols, those of nitrous acid nitrites. Of course, Morveau's innovation was attacked by both sides; the phlogistonists thought it too radical, while Lavoisier's school considered a phlogistonist no fit person to evolve any system of nomenclature at all. But Lavoisier soon felt the need of some improved machinery for pronouncing his convictions, and on Morveau's recantation the two met with this one end in view, to give names to chemical substances expressive at once of the nature and quantitative relations of their constituent elements. The compounds of oxygen with other elements, were classified as acids or oxides, according as they were acidic or basic, the name of the element from which they were derived being added; the names of acids were given the generic termination *-ique*, or *-ique* and *-eux*, when there

¹ Kopp, *Geschichte der Chemie*, ii. pp. 415 *et seq.*

were two composed of the same elements; those of the corresponding salts terminated in -ate and -ite respectively. The almost immediate acceptance of this new system throughout Europe bore testimony to its intrinsic value, a value fully recognized at the present day. In 1789 appeared Lavoisier's *Traité élémentaire de Chimie*, the herald to the world of the new, the antiphlogistic, doctrine, and of the new nomenclature.

The names of Berthollet, Guyton de Morveau, and Fourcroy deserve recognition from students of science. Morveau and Fourcroy were both zealous propagandists of the new doctrine, and in this cause their social and political position—they were both powerful in the republican tribunal—rendered them effective. The issues of their practical investigations were not, however, of a sufficiently general character to make consideration of them here opportune. On the other hand, Berthollet will ever rank with the highest.

Jean Claude Berthollet¹ was born in 1748, and his earlier manhood was spent in the pursuit of medical science, though he found time to acquire a very considerable knowledge of chemistry. From 1784, when he was made Professor at the Jardin des Plantes, his scientific work was very significant both to the technical and philosophical chemist. During the European blockade of France his intense patriotism and great gifts found vent in discovering the internal wealth of his country. Berthollet must have exhibited a singularly pleasing personality in those troubled days; able, amiable, modest, and frank, he earned the friendship of all with whom he came in contact, even of Napoleon, whom he accompanied on some of his expeditions. He died full of honours in 1822.

During the years 1785–86 Berthollet was occupied with questions concerning chlorine. Scheele had already noticed the bleaching power of the gas, and Berthollet proposed to utilize this property in the arts. Every success attended his endeavours. Chlorine water was first employed; but soon, at Javelles, its compound with potash was found more serviceable;

Berthollet,
Morveau,
and
Fourcroy.

Berthollet,
1748–
1822

Chlorine
as a
bleaching
agent.
The
chemical
nature of
the gas.

¹ Kopp, *Geschichte der Chemie*, i. p. 329.

finally, chalk and other earths were substituted for potash, and their use as absorbents was covered by patent to Tennant at Glasgow in 1798. Berthollet¹ had noticed that solutions of chlorine in water, when exposed to light, gave off bubbles of oxygen, while hydrochloric acid remained. Lavoisier had already, true to his theory of the acidic nature, declared this acid to be a compound of some unknown radical murium with oxygen, and so to Berthollet the explanation of his phenomenon seemed clear. Chlorine was obviously a higher oxygenated product of this same radical murium, and readily gave off its loosely combined oxygen, becoming muriatic acid; chlorine was merely oxymuriatic acid.

Acids that contain no oxygen. Certain oxides of the heavy metals are acidic.

More happy was Berthollet in reading the quantitative composition of prussic acid and sulphuretted hydrogen; he convinced himself that neither contained any oxygen, and was so brought to oppose the dictum that oxygen was the prime factor in producing acidity. His opposition met little encouragement, however; it was rather maintained that sulphur and nitrogen must themselves be compounds of oxygen. But we need not deplore this conservatism, for it alone has rendered the foundations of our science secure; the greater the opposition to innovation, the more trenchant and convincing have in the end been the proofs of its necessity. Berthollet's fortune it was, too, to discover that some of the higher oxides of the heavier metals behave as acids towards bases, and that ammonia is composed of hydrogen and nitrogen. But it was his great work on chemical combination that gave him enduring fame; from this work, and that of his contemporary and antagonist, Proust, chemical science has reaped manifold and lasting benefits.

The workings of chemical affinity.

It was in the year 1798 that Berthollet published his *Recherches sur les lois de l'affinité*. These *recherches* had to do with questions, first, of the fixity of chemical proportions, and secondly, of the relation between the masses and affinities of reacting units. In both cases Berthollet was attacking established opinion. All the quantitative work of Bergman and

¹ Cf. Kopp, *Geschichte der Chemie*, iii. p. 354.

Lavoisier implied a certainty that constancy of proportions was the general rule. Yet that this constancy of chemical proportions in one particular compound did not negative the existence of another compound of the same elements, had been maintained even by Stahl after his experiments on the successive additions of phlogiston to sulphur, while the constant occurrence of carbon and hydrogen, and of them only, in a large number of organic substances, had left no doubt of the fact in the mind of Lavoisier. Bergman¹ regarded affinity as a quantity fixed for each acid or base, and had arranged these in the order of their relative affinities. The greater the weight of base required to neutralize a given weight of acid, the greater the affinity of the latter; this was his root notion, and that of his contemporaries. Any idea of what we now call equivalency was entirely lacking. It was Bergman's belief that if one element, a , had a greater affinity for another, b , than had the third, c , then addition of a to the compound bc would cause the complete separation of the element b ; this assumption it was that Berthollet now combated. If, said Berthollet,² in solution, the particles of an element a come into contact with those of the compound bc , the particles of b will combine with both a and c ; and if no volatilization or precipitation occurs, equilibrium will obtain when b is divided between a and c , in a proportion dependent first on their relative affinities, and secondly on their relative masses; the product of mass and affinity he called the chemical mass. Should, however, either one of the elements b or c , or a compound of one of them with a , be volatile or insoluble, then, since the action of a would lead to the elimination of b or c from the sphere of reaction, there would be no equilibrium till the change of partner was complete, for all opposing influences to this would gradually cease to exist. In the preparation of such oxides as those of iron, Berthollet allowed that sufficiency of oxygen must be present to overcome by its affinity the cohesion of the iron particles, while, on the other hand, excess of the gas must be avoided, or the iron would

¹ Kopp, *Geschichte der Chemie*, ii. p. 312.

² *Ibid.*, ff. p. 317.

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¹ Kopp, *Geschichte der Chemie*, ii. p. 312.

² *Ibid.*, ii. p. 317.

Proust
(1755-
1826)
attacks
the views
of Berthol-
let.

scarcely overcome its elasticity; within these limits, however, the composition of the oxide would vary with the quantity of oxygen offered. And this theory, of composition varying with the quantity of the active elements present, he made general, thus attacking the very foundation of the new system of analytical chemistry.

But pregnant with valuable fruit as these speculations of Berthollet were, it cannot be denied that they were based on inaccurate experiment; and to demonstrate the extent and cause of Berthollet's error was the great service of his countryman Proust. Proust,¹ between the years 1801 and 1808, waged war on the *Essai Statique*; for examination of the oxides and sulphides of various elements had convinced him that constancy of proportions was the invariable rule. True, oxygen or sulphur might combine with an element in certainly two proportions,—later, he even allowed that these oxides might themselves combine to form bodies intermediate in composition,—but each was a compound of perfectly definite and unvarying composition. Proust demonstrated the error which underlay the old-fashioned method of determining the quantity of oxygen in oxides, of estimating the metal and calculating the oxygen by difference, proving that in many cases the bodies so examined were not oxides at all, but compounds containing hydrogen—hydroxides we now call them. He, moreover, proved that many of the bodies, on the analysis of which Berthollet had based his generalization, were not simple at all, but mixtures of substances, themselves of perfectly definite composition. So accurate were his analytical researches, and so logical his reasoning, that Berthollet was routed at every point. The law of definite chemical proportions as we now have it was the fruit of his indefatigable labours. As was natural, the discrediting of one portion of Berthollet's work led to the discrediting of the whole; but our present knowledge of the effect of increasing mass on the course of chemical change should serve to keep green the memory of the author of the *Essai Statique*.

¹ Kopp, *Geschichte der Chemie*, i. p. 358.

Proust's work is an index of the hold the quantitative method had taken on men's minds. But there were others than Proust doing much to exhibit its merits and extend its application. Klaproth,¹ the first Professor of Chemistry at Berlin, and discoverer of uranium, titanium, and zirconia, introduced the custom of publishing not merely the corrected results of analysis, but the experimental data themselves, and he laid weight on the influence which apparatus may exert by introducing impurities into the samples examined, showing how and what must be the necessary corrections made. In 1792 Klaproth, with many other German scientists, after an impartial examination of the experimental evidence for and against Lavoisier's new doctrine, seceded from the phlogistic school.

Klaproth's
work,
1743-
1817.

To Fourcroy's collaborator, Vauquelin, we owe the discovery of chromium and beryllium, the former of which he found in the form of an acidic oxide in lead spar. His work on the separation of the rare metals platinum, palladium, rhodium, indium, and osmium shows us how far the horizon of the analyst had receded. From his laboratory came most of the rarer chemical substances required by his scientific countrymen for their experimental work.

Vauquelin,
1763-
1829.

To Fischer's German translation (1802) of Berthollet's *Recherches* was appended a table of the relative affinities of bases and acids, founded on the experiments of a then little known German chemist, Richter, an account of which had been published by the author some ten years before. Richter's attention had been arrested by the well-known fact of the permanence of neutrality on mixing solutions of two neutral salts. A countryman of his, Wenzel, had previously attacked the same problem, and in 1777 had declared as his prime result, that neutrality was maintained because the quantity of acid in one salt was just that which was required to combine with the quantity of base in the other, that excess of one salt, itself neutral, was without effect on the solution. Richter,² in

Wenzel,
1740-
1793, and
Richter,
1762-
1807; the
perma-
nence of
neutrality.

¹ Kopp, *Geschichte der Chemie*, i. p. 343.

² *Ibid.*, ii. pp. 359 et seq.

his *Elements of Stoichiometry, or Art of Measuring Chemical Elements*, gave the same explanation, and as a necessary extension of this view, arrived at his law of equivalence—those weights of different bases which will saturate one and the same weight of one acid will saturate one and the same weight of another. He prepared tables of equivalency for each acid with the several bases, and for each base with the several acids, and at the same time pointed out how all these results might be comprehended in one table. This was carried into effect by Fischer¹; thus—

Bases					Acids			
Alumina	525	Fluoric acid	427
Magnesia	615	Carbonic acid	577
Potash	1605	Sulphuric acid	1000
Baryta	2222	Acetic acid	1480

Both Wenzel and Richter were before their time; Wenzel was a more accurate worker than Bergman, between whose and his own results there was therefore discrepancy; these did not, therefore, meet with any credence, nor did theoretical views based on them. Richter found the scientific world wholly occupied by questions concerning the nature of combustion, and his words went to deaf ears. But even had it been otherwise, acquiescence in his deductions would have required a recognition of the constancy of composition, a point which to many minds still waited definite settlement.

¹ Kopp, *Geschichte der Chemie*, ii. p. 365.

CHAPTER IV

DALTON'S ATOMIC THEORY AND THE WORK OF DAVY

THE first years of the nineteenth century mark a new epoch in the history of chemistry; from this time onwards the science has submitted to the dominance of a theory, whose far-reaching effects cause one to place its author, John Dalton, in the very first rank of the world's natural philosophers. Berthollet's conception of the varying composition of a chemical compound, Lavoisier's and Proust's dogmas of the constancy of chemical proportions, were equally reconciled in these philosophers' own minds with a theory of the constitution of matter, which, when applied quantitatively by Dalton, led as a necessary result to that marvellous advance in knowledge of chemical fact and theory, which has continued unhaltingly to the present day. They were all agreed on this point, that matter was discontinuous in its nature, that it was made up of finite but infinitely minute particles called atoms. The atomic theory, as it is called, can be regarded, then, as Dalton's, only in its modern application.

So far back even as the fifth century B.C., Leucippus, the Eleatic, determined that all matter was made up of certain finite indivisible particles, differing only in size, figure, position, and arrangement, by whose entangling in different combinations all known matter had been brought into being; and this theory had long been popular, though pertaining rather to vague metaphysical speculation than acknowledged physical fact. With the advance in scientific knowledge and intuition which resulted from Boyle's pioneering labours in the seventeenth century, we find the theory resuscitated in a more practical

Atoms
prior to
Dalton.

form. (Boyle explained the different chemical activities of various elements as due to the different sizes of their so-called corpuscles, and regarded compounds as produced by union of these different corpuscles.) Views not very dissimilar were held by Van Helmont and Boerhaave. In 1783 the English chemist, Kirwan, went so far as to speak of affinity as that force which holds atoms so intimately together that simple mechanical means are insufficient to separate them; while his contemporary and countryman, Higgins, writing in 1790 on the composition of sulphurous and sulphuric acids, gave it as his opinion that the atom of sulphur is combined with one atom of oxygen in the first, but with two atoms in the second. It is in view of this statement, and others similar to it, that some have regarded Higgins as the real originator of the modern atomic doctrine. But Higgins confined his attention to a small number of compounds. His conceptions were not consistent with fact; he regarded those weights of elements which combine to form the simplest compound as in general equal; and he made no attempt to seek confirmation for any theory he had in the laboratory. For long the common consent of public opinion has given the undivided honour, due to the discoverer of the great atomic generalization in its modern aspect, to John Dalton.

Dalton,
1766-
1844.

(John Dalton,¹ the son of a weaver, was born in 1766 at Eaglesfield, in Cumberland. He received his early education from his father and the schoolmaster of the Quaker school at Eaglesfield, and, at the age of twelve, he himself began to give lessons. At fifteen he removed to Kendal, where he remained twelve years, teaching in his cousin's school; all the while educating himself by the study of Latin and Greek, mathematics, and philosophy. On this latter subject he began to lecture in 1787; but in 1793 he found a wider sphere for his intellectual powers in Manchester, where he obtained the post of teacher of mathematics and natural philosophy at the new college. This college was removed to York in 1799, but Dalton remained in Manchester, where he lived by giving private lessons. The

¹ Cf. Butler, *Encyc. Brit.*, vol. 6, p. 784.

hours not spent in this way he devoted to laboratory work, the results of which, with the thoughts suggested by them, were embodied in papers read from time to time before the Manchester literary and philosophical society. The conception of the atomic theory, and the experimental work it inspired, brought Dalton prominently before the scientific public, and from 1804 onwards he was called upon to lecture in many of the principal towns of England. Advancing years brought him all the honours in turn which fall to the scientific philosopher of recognized genius. He remained in Manchester till his death, which occurred on the 12th August, 1844, retaining his simple habits to the end. Professor Sedgwick writes of Dalton as a man "with a beautiful moral simplicity and singleness of heart, which made him go on steadily in the way he saw before him, without turning to the right hand or the left and taught him to do homage to no authority before that of truth."

It has generally been supposed that the inception of Dalton's¹ atomic theory was the result of co-ordinating certain groups of phenomena under his law of multiple proportions, itself believed to be a deduction from the compositions of the hydrocarbons methane and ethylene. But the atomic theory came otherwise; the information contained in Dalton's own laboratory note-books, recently discovered in the rooms of the Manchester Literary and Philosophical Society, points to a quite different genesis of his theory. (It would appear that, prior to 1801, Dalton was already considering Newton's thesis that elastic fluids were composed of small and mutually repellent particles or atoms of matter, with a view to explaining the phenomena of diffusion. He accepted the atom, regarding its volume as made up of a hard nucleus and a surrounding heat-zone, but could only explain the inter-diffusion of gases by regarding these volumes as different for different gases, an assumption which he thought he had proved experimentally. And with this atomic theory of gases in his mind, Dalton now turned to matter in its solid and liquid states; and basing his

Origin of
the atomic
theory.
Atomic
weights.

¹ Cf. Roscoe and Haiden, *New View of Dalton's Atomic Theory*, vii. *et seq.*

calculations on the experimental values published by recognized masters, we find him scribbling on a page of his note-book, dated September 6, 1803, various numbers which were for him the relative weights of the atoms of several elements and compounds.¹

Wt. at hydrogen	1'0
„ oxygen	5'66
„ azot	4'0
„ carbon (charcoal)	4'5
„ water	6'66
„ ammonia	5'0
„ nitrous gas	9'66
„ nitrous oxide	13'66
„ nitric acid	15'32
„ sulphur	17'0
„ sulphurous acid	22'66
„ sulphuric acid	28'32
„ carbonic acid	15'8
„ oxide of carbon	10'2

Now, a careful examination of this table will show that Dalton had already recognized the law of multiple proportions by implication, as indeed he was bound, if his atoms of definite fixed weight were really indivisible; yet there is no mention of light or heavy carburetted hydrogen, the relations between which he probably did not discover till the summer of 1804.

Atomic
symbols.

The calculating of the values given involved an idea certainly new to Dalton, of the ultimate constitution of a substance. To render this more clear, he attempted, on another page of his note-book, a graphic presentment of the ultimate particles of various substances. We find nitrous oxide and nitrous gas pictured as $\textcircled{1}\textcircled{\odot}\textcircled{1}$ and $\textcircled{1}\textcircled{\odot}$ respectively, water as $\textcircled{\odot}\textcircled{\odot}$, ammonia as $\textcircled{1}\textcircled{\odot}$, gaseous oxide of carbon as $\textcircled{\odot}$ and carbonic acid as $\textcircled{\odot} \textcircled{\odot}$; in fact, the whole modern system of formulation in embryo.

The law of
greatest
simplicity.

The answer to the question why Dalton should have conceived water as composed, in its ultimate particles, of one atom of hydrogen and one atom of oxygen, rather than of

¹ *New View of Dalton's Atomic Theory*, p. 28.

these atoms in some other numerical proportions, we find in his law of greatest simplicity. In his own words,¹ "If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple, namely—

1 atom of A + 1 atom of B = 1 atom of C, binary.

1 atom of A + 2 atoms of B = 1 atom of D, ternary."

By the word "binary" he meant that C was a binary compound or atom of the second order; D was ternary, an atom of the third order. When both binary and ternary compounds of the same two elements were formed, Dalton held that one to be binary which was specifically the lighter. That in some cases, however, two elements would combine to form even more than two compounds was demonstrated in his classical researches into the combination of nitrous gas (our nitric oxide) with oxygen; "the element oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case nitric acid is the result; in the latter nitrous."

It was in December, 1803, that Dalton first divulged in lectures at the Royal Institution an outline of his new theory, but it was not till the publication of his friend Thomson's *System of Chemistry* in 1807 that it became known to the general public. By this time Dalton was applying his doctrine in the elucidation of the nature of metallic salts. Accepting the view then current of the non-decomposibility of the alkalis and alkaline earths, he estimated the weight of base which was found combined with the atomic weight of the particular acid, and, still favouring his law of greatest simplicity, wrote this as the atomic weight. Already, in 1804, he had calculated the atomic weights of various metals, of silver, mercury, iron, copper, and from time to time, as new and more accurate researches came to his notice, he altered these in accordance therewith.

Publication of the atomic theory.

¹ Cf. Dalton, *A New System of Chemical Philosophy*, 211-216, 219, 220; Alembic Club Reprints, 2, 30.

Dalton as
an experi-
menter.

Until the year 1807 Dalton had relied almost entirely on the analytical work of others, but after this date, he began to attack the problem experimentally himself, though he never attained any great proficiency. In the words of Davy, "he was a coarse experimenter, and almost always found the results he required, trusting to his head rather than to his hands."

The *New
System*.

In 1808 appeared the first volume of Dalton's *New System of Chemical Philosophy*. In its third chapter, entitled "Chemical Synthesis," he gave a detailed account of his theory, with various experimental data. The second volume of the *New System* was published in 1810, but the third not till 1827. In this work Dalton's adherence to the old school of thought is well marked; many years had elapsed since the classical demonstration by Davy of the compound nature of the alkalis, yet he still wrote atomic weights for potassa and soda. In England the *New System* found vigorous supporters in Thomson and Wollaston, and in Germany the question which it raised as to the proportion in which elements combined was attacked with avidity, though chemists for long were shy of the logical deductions from their work.

Dalton
and Davy;
their work
comple-
mentary.

While John Dalton was industriously working out the details of his atomic theory, a countryman of his, Humphrey Davy, was rapidly winning for himself an European reputation. In a manner the work of these two men was complementary; for while it was a recognition of a possible reconciliation and association between the products of speculative reasoning and facts of laboratory experiment—taking it broadly, a purely mental act—which redounded to the great glory of Dalton, it was in the main his remarkable aptitude for the technique of chemical science which placed Davy in a position of highest eminence during the first decades of the last century. The practical results of their life's work, too, were complementary; Dalton's theory of atoms provided the necessary basis for a just appreciation of the unit with which chemists had to work, while Davy's induction from his electro-chemical experiments as to the connection between affinity and chemical

function supplied the equally necessary conception of this force as an essential factor of a complicated molecular system. Both were philosophical experimenters as well as experimental philosophers, for both saw the necessity of framing some theory in accordance with known and demonstrable facts, and then working with a view to its experimental verification.

Humphrey Davy,¹ the son of an engraver, was born at Penzance in 1778. The family circumstances were somewhat straitened, and at the age of seventeen he was apprenticed to a surgeon apothecary in his native town. The natural bent of his mind was not long in showing itself; his love for chemistry he fostered by study of Lavoisier's and Nicholson's text-books; and when only nineteen he obtained through interest a post at the Bristol Pneumatic Institute, which gave him the chance of soon discovering himself to the scientific public. One of his first investigations had to do with the anæsthetic properties of nitrous oxide, a gas at the time pronounced poisonous by eminent authority. Davy experimented with it on himself—judge of the man's courage—and accurately described its effect on the human system. He then subjected himself similarly to a trial of hydrogen, nitrogen, and carbonic acid. In 1801 Davy left Bristol to become a lecturer at the Royal Institution, and two years later was elected Fellow of the Royal Society. He was soon a necessary figure in the fashionable life of the day; his auditors at the Royal Institution were numbered by the thousand; his name was on everybody's lips. He was knighted in 1811, and created baronet in 1812. A terrible mining disaster at Felling brought him an invitation from the governors of the mine to consider the conditions of such occurrences; and after an extended investigation into the nature of marsh gas in its different admixtures with air, he projected his well-known safety lamp. This is but one instance out of many of his scientific insight being turned to material advantage. Davy was elected President of the Royal Society in 1820, and died at Geneva in 1829.

¹ Cf. Burton, *Encyc. Brit.*, vol. 6, p. 845.

Davy, working at the Royal Institution, had at his command an admirable electric battery, which he was not slow to turn to account. His acute mind and wonderful manipulative power soon spread light over all those chemical phenomena associated with electrical effect, on which men's minds were bent as likely to supply the necessary clue to the inner secrets of the compound nature. Priestley, in 1772, had noticed the effect of the electric spark on the volume of ammonia subjected to its action; Cavendish, later, had employed it in his synthetical experiments; and in 1789 certain Dutch chemists had even brought about the decomposition of water through its agency. In 1781 Lavoisier and Laplace recognized an electrification of metals concurrent with their solution in acids. Galvani's experiment in 1790 and the invention by Volta of his electric cell in 1800 were new and all-important elements in the induction which went to connect chemical and electrical phenomena. Nicholson and Carlisle, using Volta's cell, immediately accomplished the decomposition of water; and Berzelius and Hisinger showed this action to be general by their decomposition of various metallic salts, discovering that while oxygen, acids and oxidized bodies appeared at the positive terminal, combustible bodies, alkalis and earths were simultaneously produced at the negative.

It had been noticed that on the electrolysis of water, traces of acid and alkali were always found at the positive and negative terminals respectively, and the opinion prevailed that this phenomenon was immediately connected with the decomposition of water as such. This gave the spur to Davy, who in 1806 felt himself in a position to state explicitly that these acids and bases were a result of the decomposition, not of the water itself, but of salts it originally contained or had dissolved from the glass of the containing vessel. He could now offer, moreover, the first intelligible and consistent hypothesis in explanation of the observed phenomena:—that which, as a function of matter in bulk, impresses our senses as electricity, associated with smallest particles, is affinity; an hypothesis based first, on the dissociation of a salt into acid and base

by passage of an electric current, and secondly, on the observed positive electrification of metals placed in contact with a solid acid and their negative electrification in contact with alkalis. It followed from this hypothesis that the electric potentials of the bodies in contact must increase with increase of temperature, till finally combination occurs, and this frequently with evolution of heat and light.

On November 19, 1807, Davy¹ gave an account to the Royal Society of his most recent work on the nature of the alkalis. He had made an attempt to decompose them by the electrolysis of their aqueous solutions, but without success; he had then passed a powerful current through solid potash fused over a flame, and had noticed a most intense light at the negative pole, due probably to the combustion of the element he was searching for. And his next experiment was decisive: "A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conducting power to the surface, was placed upon an insulated dish of platina, connected with the negative side of a powerful battery, . . . the positive pole was brought in contact with the upper surface of the alkali. On passing the current, the potash began to fuse at both its points of electric action. There was violent effervescence at the upper surface; at the lower or negative surface there was no liberation of elastic fluid, but small globules having a high metallic lustre appeared." And he had treated soda in the same manner with similar results. "It appears," he said, "that in these facts there is evidence for the decomposition of potash and soda into oxygen and two peculiar substances." To these two peculiar substances he gave the names potassium and sodium.

Decomposition of the alkalis.

Davy now turned his attention to ammonia. Reasoning from analogy, he expected to find its composition similar to that of the other alkalis, although Berthollet had found nothing but hydrogen and nitrogen result from its disruption. Davy passed ammonia over heated iron and discovered traces of moisture

The composition ammonia

¹ *Phil. Trans.*, 98 (1-44); also *Alembic Club Reprints*, 6.

in the gaseous mixture so produced; he estimated the weight of hydrogen and nitrogen formed by its decomposition, and compared this with the weight of ammonia taken. He found a difference, which he took to be due to the oxygen, whose presence was proved by the first experiment. Years later even, when there could no longer remain any doubt as to nitrogen and hydrogen being alone present in ammonia, Davy, and with him Berzelius, fell back on the hypothesis that nitrogen was itself the oxide of some element still unisolated.

The
alkaline
earths.

Analogy again demanded the inclusion of the alkaline earths among compound substances, nor did these hitherto refractory bodies long withstand such enthusiastic experimenters as Davy and Berzelius. And so the enigma of the alkalis and alkaline earths was solved. There was no shock of surprise at the demonstration of their composite nature, for long ago the fact of bases being in general oxides had suggested this to Lavoisier, and rumours of their decomposition had been frequent. It is from the year 1807, however, that we must date our real certainty of the fact.

The ele-
mentary
nature of
chlorine.

Davy next entered on a prolonged investigation¹ into the nature of oxymuriatic acid (chlorine), and as he had been successful in demonstrating the compound nature of the alkalis, so he now succeeded in proving the elementary nature of chlorine.

Henry's
opinion.

Some years before, Henry had passed an electric spark through muriatic acid gas, and had observed the liberation of hydrogen; he observed, too, that the surface of the mercury over which the gas had been collected was simultaneously attacked, evidence sufficient to him of oxidation. Henry therefore opined that dry muriatic acid must retain water in combination, a view accepted by Berthollet in 1806, and ratified by the discovery of Gay Lussac and Thénard, that the passing of muriatic acid over heated lead oxide was productive of water and muriate of lead. Lavoisier's dogma of a salt being compounded of an acidic with a basic oxide was still

¹ *Phil. Trans.*, 99, 39; *Alembic Club Reprints*, 9.

almost universally upheld, and Gay Lussac and Thénard were quite consistent therefore in believing muriate of lead composed of oxide of murium with oxide of lead, and the water formed to be that originally present in the gaseous acid. Again, it was well known that when metallic potassium was brought into contact with muriatic acid, muriate of potassium was produced with evolution of hydrogen. This hydrogen must surely have come from the water of the muriatic acid, whose oxygen combined with potassium to produce the basic radical of the resulting salt.

On December 15, 1808, Davy read the first of his memorable papers on the nature of oxymuriatic acid before the Royal Society; he was still a believer in the compound nature of the gas, but with each succeeding paper he grew less and less convinced of this, and finally, in November, 1810, declared the gas elementary, naming it chlorine. By no means whatever could Davy abstract the oxygen from oxymuriatic acid; a succession of electric sparks produced no effect, neither did strongly ignited carbon. Were the gas oxidized, muriatic acid, phosphorus and sulphur might be expected to combine with the oxygen and liberate the muriatic acid; no such result had been obtained, however, and the oily liquids which were produced only yielded muriatic acid on the addition of water. The oxymuriatic acid, when passed over oxides of potassium, barium, and other metals, produced muriates with evolution of precisely that amount of oxygen contained in the oxides. Referring to this experiment, Davy remarks, "It is contrary to sound logic to say, that the exact quantity of oxygen is given off from a body not known to be compound, when we are certain of its existence in another." Chlorine, then, was an element, as Gay Lussac and Thénard had allowed possible some years before, though, in deference to Lavoisier's doctrine, they had chosen the more conventional alternative.

This work of Davy's gradually brought conviction, and by the year 1820 his theory of the nature of chlorine was regarded as the one possible. By it was induced the first considerable modification of Lavoisier's system, for oxygen could no longer

Davy's work.

Oxygen no longer the sole acidifying agent.

be held the sole acidifying agent. Davy had recognized this immediately, and had spoken of all salts as haloid, the acidifying unit in one case being compound and in another elementary.

Discovery
of iodine
and
bromine.

A French saltpetre manufacturer, Couutois, in 1811 discovered a strange substance in the soda obtained from sea plants; he told his discovery to Clément, who showed the body in question to Davy. Davy soon demonstrated its elementary nature, and Gay Lussac, after a complete investigation of iodine, as he called it, and its compounds, succeeded in showing its marked likeness to chlorine. Bromine was discovered by Balard, in 1826, in the mother liquor of sea-water. Hydrofluoric acid resisted all attempts to isolate its radical, but Ampère's suggestion, that it was constituted similarly to muriatic acid, found general acceptance.

The work of Davy had no bearing on the atomic system of Dalton. While admitting the possibility, and even likelihood, of matter being composed of smallest particles, Davy saw no reason to accept what he called Dalton's proportion numbers, as expressing the relations between the weights of these particles. But we now come to consider a body of research, the results of which in their later application proved of vital importance to the fortunes of the atomic theory.

Gay
Lussac
and the
volume
ratios of
combining

In the December of 1808 Gay Lussac¹ read a paper before the Société d'Arcueil on the results of an investigation into the nature of combination between different gases. The small specific gravity of gases had long ago led to their quantitative estimation in terms of volume; thus we find Priestley measuring the volumes of ammonia and muriatic acid, Cavendish those of hydrogen and oxygen, and Berthollet those of nitrogen and hydrogen, which combine to form their respective compounds. And more or less simple relations had been found to obtain between these volumes, a fact, however, deemed of little importance. Gay Lussac had early made his mark as an expert physicist by his recognition in 1802 of the identical behaviour

¹ Cf. Alembic Club Reprints, 4 (8-24).

of all gases under the influence of increasing or decreasing temperature. In 1805, after careful research in conjunction with Humbolt, he was able to announce that it was precisely two volumes of hydrogen which combined with one volume of oxygen to form water, a result sufficiently significant to make him curious about other phenomena of a similar character. In 1808 his mind was made up. "I prepared fluorboric, muriatic, and carbonic acids," he said, "and made them combine successively with ammonia gas. . . . We may conclude that muriatic, fluorboric, and carbonic acids take their own volume exactly of ammonia gas to form neutral salts, and that the last two take twice as much to form sub-salts." He then quotes Berthollet's work on ammonia, and the volumetric ratios of sulphurous acid and oxygen in sulphuric acid, and of carbonic oxide and oxygen in carbonic acid, and finds all covered by the one general law, "gases combine in very simple ratios." Knowing these ratios, and the specific gravity of each of the combining gases, Gay Lussac was able to calculate the specific gravities of compounds resulting from their union; the confirmation of these values by experiment gave him and others complete confidence in the truth of his generalization.

That there was analogy between his law of volumes and Dalton's theory of combination by atoms was soon perceived by so acute a philosopher as Gay Lussac; he saw in it proof that both were true. Dalton, on the other hand, repudiated any such proof. In the second volume of his new system he writes, "Gay Lussac's notion of measures is analogous to mine of atoms; and if it could be proved that all elastic fluids have the same numbers of atoms, or numbers that are 1, 2, 3, etc., the hypothesis would be the same, except that mine is universal, and his applies only to elastic fluids." But Dalton had his own reasons, as we have seen, for believing the ultimate atoms of different substances different in magnitude; moreover, he denied the experimental evidence for Gay Lussac's hypothesis.

The connection between Gay Lussac's law of volumes and Dalton's theory of atoms was discovered in 1811 in an essay

Gay
Lussac
and
Dalton.

Avoga-
dro's hy-
pothesis.

by Amadeo Avogadro,¹ "on a manner of determining the relative masses of the elementary molecules." Avogadro at once divined that the explanation of the law of volumes must lie in the numerical relations of the smallest particles, and as the only obvious hypothesis he assumed the number of these smallest particles in equal volumes of all gases to be the same. Avogadro was thus at once met by a difficulty which had puzzled Gay Lussac; the latter had discovered the density of carbonic oxide to be less than that of oxygen, though the carbon with which the oxygen had combined was a solid substance. Avogadro overcame this difficulty by assuming the smallest particle (molécule) of an elementary gas to be made up of a number of still smaller particles (molécule élémentaire), in general two, though in some cases possibly four or eight, and showed how relative densities of gases calculated on this assumption completely agreed with values determined experimentally. So he could now criticize the weights assigned by Dalton to various atoms; and this he did, showing how in no way did Dalton's law of greatest simplicity necessarily give results agreeing with those founded on his own proved hypothesis; that in the case of water, for example, the numerical ratio of hydrogen and oxygen atoms must be 2 : 1, and not 1 : 1. Consideration of carbonic acid led him to speculate on the density of carbon as gas, and he arrived at the value 11.36, that of hydrogen being taken as unity. Some idea of his mental grasp of the problems before him may be obtained from the following passage: "There is, however, one difficulty in this supposition [that the density of carbon = 11.36], for we give to the molecule of carbon a mass less than that of nitrogen and oxygen, whereas one would be inclined to attribute the solidity of its aggregation at the highest temperatures to a higher molecular mass, as is observed in the case of sulphuric and phosphoric radicals." This difficulty he disposed of, arguing from the analogy of chlorine and mercury, one of which was already gas, and the other easily vaporizable. It is curious that neither Gay Lussac nor Avogadro brought

¹ Cf. *Alembic Club Reprints*, 4 (28-51).

forward the identical behaviour of all gases under change of pressure and temperature as evidence in support of their views.

Avogadro's conclusions met with scant respect from his Ampère. brother chemists; they were regarded as purely speculative, and so without bearing on the practical questions at issue. Moreover, a differentiation between smallest particles, physically smallest and chemically smallest, was held to complicate the question rather than conduce to its solution. So little regarded, indeed, was the paper of Avogadro, that Ampère,¹ in 1814, could publish as his own, under cover of a letter to Berthollet, conclusions very little different from those detailed. Ampère met with as little sympathy as Avogadro.

¹ Cf. Kopp, *Entwicklung der Chemie*, p. 354.

CHAPTER V

BERZELIUS AND THE DEVELOPMENT OF THE ATOMIC SYSTEM.

Berzelius
and the
develop-
ment of
chemical
science.

It was thirty years since Lavoisier had entered on his anti-phlogistic campaign; complete success had awarded his efforts; and the weapons he had forged, of homage to experimental fact and scepticism of so-called established truths, were become the common property of scientific men. Lavoisier had felt that constancy of chemical proportions underlay phenomena; and Proust, after demonstrating the weakness of Berthollet's position, had shown this to be, indeed, a fundamental truth of our science. And now there was Dalton's theory of atoms, with its corollary, the law of multiple proportions, while the rapidly extending knowledge of the disintegrating power of electricity supplied not only a host of new elements, but a theory to co-ordinate the most widely separated chemical facts. The spirit of order was creeping in on all sides to become incarnate during the early years of last century, in Berzelius. Though scientific societies, with all the accompaniments of printed transactions and foreign membership, were rapidly multiplying, news of discovery did not travel very fast, and, coming from all quarters of Europe, left with the superficial a rather kaleidoscopic impression of brilliant fragments. But for Berzelius there were no fragments; each fresh discovery came like a cast from the mould, needing but a touch here and a touch there, to fit exactly the body which with tremendous energy he had set himself to fashion. Proust's law of constant proportions—on how small a capital of experiments it was founded! Berzelius confirmed it by a wealth of brilliantly achieved results. Dalton's

theory of atoms—outside England it was curiously regarded as an ingenious speculation without serious relation to fact! Berzelius received it, nourished it, and finally forced it full fledged on the world as the soul of all progress. The relation between electricity and material substance—Davy, true, had glimpses of the light, but it was Berzelius who first grasped it, and utilized it to illuminate the whole domain of chemistry! Berzelius was a man of lofty ideals, and of strength of mind and body to pursue his ideals; hence came great work, and, as a necessary consequence, great power over his contemporaries. For thirty years he ruled as an autocrat, and his sense of co-ordination became disseminated through the whole chemical world; his chemistry was our chemistry in strenuous youth.¹

Jacob Berzelius¹ was born in 1779; his father was a school-master at Westlösa, in Sweden, and the boy in course of time went to Upsala to study for the medical profession. He was but twenty when he undertook his first extensive chemical research—an investigation of the medicinal springs at Medevi, in the neighbourhood of his birthplace. Shortly afterwards, in 1802, in conjunction with Hisinger, he set to work to examine the action of the electric current on various salts, with the most far-reaching results for himself and his science; for almost immediately the desire to keep so promising a student in Stockholm prompted the authorities to create for him a new academic position, that of assistant professor of chemistry and pharmacy to the medical faculty there. His star was in the ascendant; with the growing recognition of his great powers came offers of public positions; and in 1807 he was finally installed in the chair of chemistry and pharmacy. This he continued to adorn for five and twenty years, and meanwhile the brilliancy of his work met with full recognition both at home and abroad. On the accession of King Karl Johann, in 1818, he was ennobled; while seventeen years later, on the occasion of his marriage, he was created Baron. Foreign

Berzelius,
1779-
1848.

¹ Cf. Kopp, *Geschichte der Chemie*, i. p. 390; also Berzelius-Wöhler, *Berzelius-Kiebig, Briefwechsel*.

societies entered his name with pride on their member sheets; the directors of the Swedish iron works voted him a pension. Worthily had he maintained the scientific reputation of his country, gained by the labours of Scheele and Bergman.

Berzelius' character was of too solid a type to be changed by the world's applause; very warm and enduring was his friendship for those who by their life and work showed themselves worthy; very scathing was his criticism on persons or things savouring of charlatanry or deceit. Mentally cautious, he was exceedingly conservative in his opinions: "Do not form convictions without the strongest evidence; do not forsake them lightly." Such was the philosophy behind his life's work. Chemical science was in a state of flux throughout his career; to his conservatism in great measure we owe that solid body of scientific fact which slowly won conviction during the decades succeeding his death.

Berzelius' great reputation drew many aspiring students from all countries to his house in Stockholm, where for a time they might work side by side with the master, assimilate something of his method and enthusiasm, and go forth to spread far and wide his doctrines. To some few months so spent may be traced much of the subsequent fame of Gmelin and Mitscherlich, the brothers Rose, Wöhler, and Magnus. "The laboratory¹ consisted of two ordinary rooms furnished in the simplest possible way; there were no furnaces, or draught cupboards; neither gas nor water service. In one of the rooms were two common deal tables; on one of these worked Berzelius; the other was intended for me [Wöhler]. On the walls were a few cupboards for the reagents; in the middle was a mercury trough, while the glass-blower's lamp stood on the hearth. In addition was a sink, with an earthenware cistern and tap, standing over a wooden tub, while the despotic Anna, the cook, had daily to clean the apparatus. In the other room were the balances, and some cupboards containing instruments; close to was a workshop fitted with a lathe. In the neighbouring kitchen, in which Anna prepared the meals, was a small

¹ From Thorpe's *Essays in Historical Chemistry*, 1st ed., p. 240.

but seldom used furnace, and the never-cool sand-bath." And over all presided the "well-clad, portly, vigorous-looking" Berzelius.

If the sand-bath was seldom cool in the laboratory, the pen was seldom dry in the study. Berzelius' literary activity was marvellous. A never-ceasing succession of papers, containing accounts of his laboratory work or criticisms on that of others, appeared in the various scientific periodicals; a yearly *résumé* of progress in the physical sciences was furnished to the Stockholm Academy; while his numerous complete works on chemistry and kindred subjects spoke even more strongly of his unflagging zeal. But in the writing and revising of these, to meet the requirements of advancing knowledge, even Berzelius was impressed with a sense of the exactions of labour. "The devil may write text-books of chemistry," said he, "for every few years the whole thing changes." And when the day's work, laboratory and literary, was put away, Berzelius still clove to his desk. His friends were many, his correspondence great, for his was not a lukewarm nature. An account of his latest research, a witty criticism of some savant's inconsistencies, a paternal homily on perseverance, a brotherly solicitation over a friend's misfortunes, and all harmoniously combined, must have rendered his letters a delight to their many recipients.

Berzelius' *Lehrbuch der Chemie*, begun in the year 1808, Berzelius' *Lehrbuch*. fixed the type for works of the kind. It appeared in five editions, and was disseminated over Europe in its various translations. It was characterized by succinct statements of fact, scientific method and omniscience. His opinions¹ on the standard English and French text-books of the day were by no means flattering, the first "compiled without knowledge of anything not accomplished in England by Englishmen," the last "restricted to co-ordination of French scientific literature alone." "How far they rank behind the German!" he adds.

When Berzelius, about the year 1808, began his investigation Berzelius and the

¹ Berzelius-Wöhler, *Briefwechsel*, i. p. 267.

laws of
chemical
combina-

of chemical proportions, he was well aware of Proust's conclusions, also of Dalton's newly discovered law. This law of multiple proportions was a generalized expression of the fact, first noticed by Proust, that where two different compounds of the same element existed, there was a definite jump in the proportions of the one element combined with the constant weight of the other. If Dalton was right, there was gained, as Berzelius saw, a very important step towards the consummation of his science. But was he right? Was the law of multiple proportions all-embracing? Might it not be that the jumps in composition were often ordered merely by the character of the particular elements combining? Here was good ground for careful experiment, experiment which, too, must nearly touch another question Berzelius had much at heart. In his reading, preparatory, doubtless, to the compilation of his *Lehrbuch*, Berzelius had come across Richter's oxygen law, and in confirmation of it had himself shown that those weights of bases which saturated the same weight of muriatic acid contained the same weight of oxygen; that such weights would, moreover, saturate the same quantity of sulphuric acid, if one composition for the acid were consistently followed. But the two series of bases so obtained did not completely correspond; thus the numerical relation between the weights of two bases, which saturated the same weight of muriatic acid, was not necessarily that which held between those which saturated the same weight of sulphuric acid. Why was this?

The law
of multiple
propor-
tions.

The first position fortified was the law "per saltum" of Proust as it affected the oxides of lead; these he found to contain oxygen combined with the same weight of lead in the proportions $1 : 1\frac{1}{2} : 2$. The oxides of sulphur next came under examination, and after an accurate analysis of their compounds with barium oxide, Berzelius found that the one contained just one and a half times as much oxygen as the other combined with the same weight of sulphur; and, incidentally, that the sulphates held four times as much oxygen as the basic oxide they contained. Then followed accurate analyses of the oxides, sulphides, sulphates, and chlorides of copper and iron. In

every case the percentage composition was calculated, and this with salts in terms of base and acid.

Berzelius was at the time a steadfast believer in the compound nature of chlorine; indeed, he did not give in to Davy's opinion till 1820. His method of handling the various compounds containing this substance is therefore the more interesting. An example will serve to make clear this method and discover the logical basis of all Berzelius' analytical labours. It must be remembered that Berzelius' work with Hisinger on the disintegrating power of the voltaic current had already convinced the former of the dualistic character of salts; the two parts combined were both oxides—the one base, the other, as Lavoisier had suggested, acid.

Berzelius' method of quantitative analysis.

"Analyses of Silver and Barium Muriates.

"1. I dissolved 3 grms. pure silver¹ (reduced from silver muriate and preserved in the molten state for a considerable time to free it from carbon) with nitric acid in a small weighed flask, added pure muriatic acid, and evaporated to dryness; again added muriatic acid, and finally fused the product in the flask. The colourless horn silver so obtained weighed 3.98 grms., which showed that 100 parts of silver had taken up 32.7 parts of oxygen and muriatic acid—that, in fact, 100 parts of silver chloride contained 75.358 parts of silver.

"2. From 10 grms. of silver, purified and treated in precisely the same manner, I obtained 13.275 grms. of molten silver muriate. From this experiment, then, it appears that 100 parts of silver muriate contain 75.3296 parts of silver.

"3. Ten grammes of carbonated baryta were dissolved in muriatic acid in a weighed flask; the solution poured into a weighed platinum crucible, carefully evaporated to dryness, and ignited. I obtained 10.56 grms. of barium muriate.

"4. The same experiment was repeated, and this time the mass was left in the flask, and there dried and ignited; again I obtained 10.56 grms. of barium muriate.

¹ Berzelius: Versuch, die bestimmten und einfachen Verhältnisse aufzufinden. *Astwald's Klassiker*, No. 35, p. 24 (1811-1812).

"Now, since 100 parts of carbonated baryta contain 78.4 parts of baryta, the 10.56 grms. of barium muriate must contain 2.72 grms. of muriatic acid.

"But $10.56 : 2.72$ as $100 : 25.75$; therefore 100 grms. of anhydrous barium muriate must contain—

25.75 grms. of muriatic acid, and
74.25 grms. of baryta.

"5. The 10.56 grms. of barium muriate obtained in the fourth experiment was dissolved in water and precipitated with silver nitrate. The molten horn silver weighed 14.55 grms. Silver muriate must therefore contain—

18.7 parts of muriatic acid, and
81.3 parts of silver oxide,

from which it follows that 100 parts of silver oxide contain—

92.67 parts of silver, and
7.33 parts of oxygen."

The corresponding values accepted at the present day are 93.09 and 6.91 respectively. Here is, thus, an error of approximately but 0.4 per cent., and this in an indirect determination!

His vast quantity of experimental work, carried out on such lines as these, gave Berzelius authority to state explicitly that when any two bodies, A and B, combine with one another in different proportions, a very simple relation is to be traced between the weights of the one element combining with the constant weight of the other; thus 1A with 1B (A and B represent the minimum quantity of either element) 1A with $1\frac{1}{2}$ B, 1A with 2B, or 1A with 4B. Here, then, was Dalton's law of multiple proportions verified, and verified too in its application to all inorganic compounds, solid, liquid, and gaseous. It must be observed that so far Berzelius had made no attempt at formulation; he was merely concerned with minimums and maximums of elements in combination, and the relations between them.

That other law, foreshadowed by Richter—the law of reciprocal proportions—was also established; if two substances,

The law of
reciprocal
propor-

A and B, have affinity for two others, C and D, the amounts of C and D which saturate a constant weight of A are in the same ratio as those which saturate a constant weight of B. This reciprocal relationship enabled Berzelius, by calculation, to check results obtained in the laboratory; it led him, moreover, at times to analyze bodies whose composition had hitherto been regarded as finally settled. /

Among the many substances analyzed by Berzelius were those containing nitrogen—nitrates, nitrites, and ammoniacal salts. The experimental part of the work offered no considerable difficulty; he had only to ignite a known quantity of barium nitrate, and weigh the oxide left, to learn that 100 parts of nitric acid saturated 140.73 parts of barium oxide; and by the law of reciprocal proportions, this relation between nitric acid and baryta would suggest that between the same acid and any other base. But the composition of nitric acid¹ itself was by no means obvious. Was nitrogen to be regarded as elementary or not? Analogy between the salts of ammonium and those of the alkali metals, and still more between the amalgams which ammonia and these metals respectively form with mercury, made it possible that the bases of potash and ammonia were of one type. On the other hand, Gay Lussac had decomposed ammonia into nitrogen and hydrogen, and was now maintaining that these were its sole and elementary components. If this was so, whence came its basic properties, for neither nitrogen nor hydrogen showed any, and how could any two elements combine to form a compound more electropositive than either? No; Berzelius was convinced that the base of ammonia, like that of potash, was metallic; that this base, having combined with oxygen, then combined with water to form the well-known alkaline gas. When ammonia formed salts, it was necessarily this oxide which combined with the acid, also an oxide; and the evolution of water on heating ammoniacal chloride with anhydrous lime was merely consequent on the salt containing water of crystallization. He offered the

The composition of ammonia and nitric acid.

¹ Cf. Berzelius, *Ostwald's Klassiker*, No. 35, p. 97 (1811-1812).

following values as representing the composition of ammoniac chloride :—

Muriatic acid	49.58
Caustic ammonia	31.95
Water	18.5

Berzelius' conception of nitrogen as the oxide of an unknown element ammonium received confirmation from yet other and quite different data. An analysis of barium nitrate yielded the following :—

Nitric acid	100 parts
Baryta	140.73 parts.

Thus 100 parts of nitric acid saturated that amount of base which contained 14.66 parts of oxygen. But Berzelius had discovered that, in a salt, there always obtained some simple relation between the oxygen contents of base and acid ; and after Gay Lussac, 100 parts of nitric acid were composed of 30.5 parts of nitrogen and 69.5 parts of oxygen (Gay Lussac had mistaken nitrogen peroxide for nitrogen pentoxide, and not unnaturally, for on combination with water it forms nitric as well as nitrous acid). But the ratio between 69.5 and 14.66 was not a simple one, and the only explanation of the inconsistency between law and experimental fact lay in the assumption that the nitrogen of nitric acid itself contained oxygen. This question of the nature of nitrogen has been treated somewhat fully, considering the scope of this work ; for the method of its logical and experimental treatment at the hands of Berzelius serve to give one a real insight into the theoretical and practical problems, which awaited solution at the beginning of last century. A thorough grasp of history is only possible when the conditions of work and thought at the time of action are appreciated ; the student must be in sympathy with his subject.

By the end of the year 1812 Berzelius had published analyses covering the whole domain of inorganic chemistry, and had achieved his goal ; constancy of proportions as a law could take its place beside that of gravitation. He had set a

standard too—one of indomitable perseverance, experimental accuracy, and intellectual intuition.

On August 1, 1812, Berzelius,¹ in a letter to Dalton, writes, ^{Berzelius and the atomic theory.} "I am much obliged for your present of the new system of chemical philosophy, which gives me the more pleasure as I have long wished to know your views on a chemical point which has long interested me;" and no wonder, for in his hands was now the key to the problem whose character he had spent so many busy years in elucidating. The laws of constant and multiple proportions had been to him by no means axiomatic; had possessed, indeed, no *a priori* probability until read in the light of the atomic hypothesis. But from this time forward matter to Berzelius was atomic, built up of smallest particles, these spherical and of equal magnitude, endowed with electric charges, which when different induced combination and consequent electric neutralization. To the ultimate particles of a body so produced he applied the term "compound atom of the first order;" to those resulting from the combination of two "atoms of the first order," the term "compound atom of the second order." Such compound atoms of the first order as contained more than two elements were only to be found in organic substances, and were called by him organic. The task before him was plain. He must determine, with the greatest possible exactitude, the relative weights of the smallest indivisible particles or atoms of the elements, that from an analysis of any substance he might obtain a real presentment of its ultimate structure. Already he had estimated the gravimetric minima of different elements in combination, and had shown that when two such elements unite in more than one proportion 1A combines with 1B, $1\frac{1}{2}$ B, 2B, or 4B, where A and B represent such minima; but was he therefore any nearer the relation of their atomic weights? What guarantee had he that these minima were not multiples or sub-multiples of the values he sought? Here was the same difficulty which had before taxed Dalton, who was fain to answer with his law of greatest

¹ *New View of Dalton's Atomic Theory*, p. 156.

simplicity. Berzelius' philosophic insight was too keen to allow any such compromise; he required further data before he could attack his problem with any sense of security.

Berzelius
employs
Gay
Lussac's
law of
volumes.

The law of volumes enunciated by Gay Lussac in the December of 1808 came to Berzelius as the necessary "deus ex machina," a deus which, while helping to cut the Gordian knot of the relationship between the weights of atoms and the minimum weights found by analysis, received its amplest theoretical vindication in the existence of these atoms. There seemed no reason why laws which held for the combination of gases should not hold equally for that of liquids or solids. But it was difficult to believe that there were not as many atoms in one simple gas as in another, volume for volume—to believe, for example, that one volume of hydrogen contained only half as many atoms as one volume of oxygen, though, indeed, one volume of oxygen did combine with two volumes of hydrogen. It was difficult, therefore, to do otherwise than assume the water atom composed of two atoms of hydrogen and one atom of oxygen.

Volume
weights.
Composition of the
carbon
oxides.

If, now, this equality in the number of atoms present in equal volumes of different simple gases was a fact, one had only to determine the relative specific gravities of such gases to obtain the relation of their atomic weights. Let us do this, said Berzelius;¹ and, as an outward and visible-sign of our dependence on established fact, let us henceforth speak, not of atomic weights, but of volume weights. True, we know only two definitely simple gases; but analogy, in the light of our laboratory experience, will enable us to postulate concerning the composition of many substances, as we can now do with absolute certainty concerning the compounds of hydrogen and oxygen alone. Thus consider the oxides of carbon. Carbon unites with one or with two volumes of oxygen to form two volumes of the lower and higher oxides respectively; there seems a general tendency for two volumes of a gas to combine without condensation; and why, in the case of the higher oxide

¹ Cf. *Sur la Théorie des Proportions Chimiques*, p. 47. Berzelius, Paris, 1819.

of carbon, should we not assume that one volume of carbon combines with two volumes of oxygen, just as one volume of oxygen combines with two volumes of hydrogen? If this is the truth, then the lower oxide of carbon must result from the combination of one volume of carbon with one volume of oxygen. But what holds good for the oxides of carbon will probably hold good for the oxides of other elements; they will be produced by the combination of one volume with one, two, or three volumes of oxygen. Some chemists will protest and say, Why one volume, and not two or three, with one, two, or three of oxygen? Because, if two, it might be three or four, or nine or ten; and, theoretically, it is extremely probable that such complicated atoms would break down at once into those more simple.

Now, just as carbon forms two oxides, so also do the metals copper, mercury, and gold; and by experiment it is found that of these oxides, those in every case containing the smaller quantity of oxygen, their atoms being composed of one volume atom of metal to one volume atom of oxygen, exhibit the weakest affinities; the higher oxides—those of marked basic character—will contain one volume atom of metal and two volume atoms of oxygen. Here is ground for generalization; it is the more powerful bases, the oxides of potash and soda, those of barium, strontium, and calcium, whose ultimate atoms contain two volume atoms of oxygen to one volume atom of metal. The combination of three volume atoms of oxygen with one volume atom of aluminium, and three or six volume atoms with one of chromium, to produce in every case substances of weakly basic if not actually acid character, makes us suspect other metallic oxides of similar properties to be analogously constituted.

The
metallic
oxides.

While the weights of oxygen combined with one weight of carbon to form its two oxides are in the ratio 1 : 2, those combined with sulphur are in the ratio 1 : $1\frac{1}{2}$. Allowing, then, that not more than one volume atom of sulphur can be present in one atom of either oxide, there must be two and three volume atoms of oxygen in these respectively, for $1\frac{1}{2}$ volume atoms of oxygen is an unthinkable quantity. These results lead one to

The oxides
of sulphur.

suppose that there must or may exist a third oxide of sulphur hitherto undiscovered, into whose composition enter one volume atom of sulphur and one volume atom of oxygen.

Here, then, we have the theoretical basis for Berzelius' first table of volume weights (1813). The values are given relative to that of oxygen taken as 100—a course which had already been adopted by Thomson and Wollaston in England. The relative number of elementary volumes present in the ultimate atoms of the compounds analyzed are taken as known on the principle above discussed, and their weights calculated from analyses already published, or from others made for the special purpose of this calculation. To the following selection from Berzelius' table are appended values calculated from those given on the assumption that $O = 8$; the reader will thereby more easily gauge Berzelius' accuracy. The formulæ supply the theoretical reason for the numbers chosen.

		$O = 100.^1$		$O = 8.$
Hydrogen	6.64 (H^2O)	0.53
Carbon	75.1 ($C + O$)	6.01
Sulphur	201.0 ($S + 2O$)	16.08
Iron ...	* ...	693.6	{ the lower oxide } ($Fe + 2O$)	54.3
Copper	806.5	{ the higher oxide } ($Cu + 2O$)	64.52
Silver	2688.2 ($Ag + 2O$)	215.06
Potassium	978.0 ($K + 2O$)	78.24
Chromium	708.0	{ the basic oxide } ($Cr + 3O$)	56.64

Chemical notation.

Berzelius was meanwhile evolving a system of chemical notation which, in his words, "might facilitate the expression of chemical proportions, show briefly and clearly the number of elementary atoms in each compound, and after the determination of their relative weights, present the results of each analysis in a simple and easily retained manner." The atom of each element was implied by the initial letter of its latinized name, a second letter being added when two elements had names beginning with the same capital. An index number

¹ Kopp, *Entwicklung der Chemie*, p. 368.

was added in cases where more than one atom were present. A presentment of the two oxides of copper was thus supplied by the 'expressions $\text{Cu} + \text{O}$ and $\text{Cu} + 2\text{O}$. This method proved impracticable, however, where atoms of the second or third order were concerned; $(\text{Cu} + \text{O}) + (\text{S} + 3\text{O})$ was almost as cumbrous as one of Dalton's old diagrammatic formulæ, so for such bodies he suggested $\text{Cu} \overset{\cdot}{\text{S}}, \text{Cu} \overset{\cdot}{\text{S}}^2$, the several dots standing for atoms of oxygen, and the index signifying two molecules of the sulphuric acid radical. As an example of his formulation of an atom of the third order, we may take alum, $(\text{K} \overset{\cdot}{\text{S}}^2 + 2\text{Al} \overset{\cdot}{\text{S}}^3) + 48\text{H}^2\text{O}$. But Berzelius by no means regarded these formulæ as final, nor the volume weights based on them; he was constantly haunted by the idea that possibly such oxides as those of sulphur might be better expressed as $\text{S} + \text{O}$ and $2\text{S} + 3\text{O}$, than by the formulæ he had adopted. His table of volume weights was presented rather with the object of offering to the practical chemist data for the calculation of necessary quantities, than of dogmatizing on what he felt must remain a question for each chemist to settle to his own satisfaction.

One must not imagine that in the determining of the combining values of the elements Berzelius held the field alone. Both in England, the home of the atomic theory, and in France, the birthplace of the rigorous quantitative system, the work of the laboratory was directed in a measure towards this end. But there was a feeling abroad that theory must be kept within bounds; the downfall of phlogiston was too recent not to point a moral, and the atomic theory seemed insidious. Davy thought it safer to speak of proportion numbers, numbers which were experimentally verifiable and independent of any theory whatsoever. Wollaston, too, took the same point of view in drawing up his table of "chemical equivalents"—the corresponding quantities of different substances—copies of which found their way into most of the laboratories of Europe. These equivalent weights were in part derived from experiments conceived in the spirit of Richter, and in part from measurements

Attitude of others towards the conception of atomic weights.

suggested by Gay Lussac's law of volumes; they were presented with their logarithms, and the table was accepted as a species of chemist's ready reckoner. Still, neither Davy nor Wollaston was blind to the appositeness of Dalton's theory to their facts, though they refused official sanction to associating one with the other. Similarly in France and Germany, Gay Lussac and Gmelin, while exercising themselves in the determination of stoichiometrical relations, appeared equally anxious to avoid any appearance of theoretical bias. Gay Lussac proposed the term "rapport" for the values obtained, admitting, however, the suitability of "proportional numbers," estimating these on the one hand from the results of ordinary gravimetric analysis, and on the other by deductions from his law of volumes. Gmelin thought that "mixing weights" best expressed the meaning he would convey by his numbers, but admitted their somewhat arbitrary character, owing to a difficulty in knowing when one might assume one and when two "mixing weights" of one element to be combined with one "mixing weight" of a second in any given compound.

Thomson's
atomic
weights.

Of those chemists who approached the problem in the spirit of Dalton, the Englishman Thomson was the most conspicuous; and shortly before the publication of Berzelius' scheme of atomic weights, he had printed in his *Annals of Philosophy* a table identical with it in character. Many of the values given, however, differed radically, being multiples or sub-multiples of those of Berzelius. The latter was guided by Gay Lussac's law of volumes in his choice, but this law was of little assistance to Thomson, who, like Dalton, looked on it as a mere ingenious speculation. The law of greatest simplicity furnished him with what he piously believed firmer foothold—in any compound the smallest particle will contain one atom, and one atom only, of at least one of the components—so he made it his object to determine the smallest weights of elements ever found in their compounds. It seemed to him, as to Wollaston and Berzelius, most convenient to accept the atomic weight of oxygen as the unit, for it was generally the oxides which supplied the numerical data for calculation; and, again,

the part played by oxygen in its compounds was so all-important. Moreover, having drawn up his table according to this scheme, he lighted on a fact which appeared most significant, and which would not have been obvious had hydrogen been accepted as the standard element. The following were some of his values :—

	O = 1.000.		O = 8.
Hydrogen ...	0.132 (HO)	...	1.06
Nitrogen .	0.878 (NO)	..	7.02
Oxygen ...	1.000	...	8.00
Sulphur ..	2.000 (SO)	...	16.00
Iron ...	6.666 (FeO ₂ and FeO ₃)	...	53.33
Copper ...	8.000 (CuO)	...	64.00
Lead ...	25.974 (PbO ₂ , PbO ₃ , PbO ₄)	...	207.79
Mercury ...	25.000 (HgO)	...	200.00
Potassium ...	5.000 (KO and KO ₂)	...	40.00

Five of these atomic weights were simple multiples of that given to oxygen. It is true that Dalton's atomic weights had all latterly been expressed by whole numbers—multiples, therefore, of that of hydrogen—but this had merely implied a confession of difficulties in analysis. No such confession could be conveyed by Thomson's tables; for here values were given to three places of decimals, which precluded all possibility of the simple relations indicated being due to mere coincidence. No developments followed, however, though some idea of the ultimate unity of the elementary substance must have been latent in Thomson's mind, as judged by his subsequent attitude to the question of a one primordial substance.

In the year 1815 there appeared in the *Annals of Philosophy* a paper by an anonymous author, on the numerical relation between the specific gravities of elements in the state of gas and their atomic weights. These specific gravities were directly determined in the case of oxygen, nitrogen, and chlorine, and indirectly for other elements, on the assumption that the specific gravities of these bore the same relation to one another as did their atomic weights. The numerical values advanced for these atomic weights were deduced partly

Prout's
hypothesis.

from the experiments of others, partly from the writer's own. Their accuracy may be judged by the following :—

H = 1	Ca = 20
C = 6	Na = 24
N = 14	Fe = 28
P = 14	Zn = 32
O = 8	Cl = 36
S = 16	K = 40
Ba = 70	I = 124

Now, according to the author, these values also represented the relative specific gravities of the corresponding elements; and in a paper published the following year, in which the author discovered himself to be an English physician, called Prout, he suggested that the specific gravity and atomic weight of hydrogen should be given as 1, that a knowledge of the atomic weight might carry with it a knowledge of the specific gravity too. Prout observed that all these values were whole numbers, and did not long delay his conclusion; for since there is no effect without its cause, he could only assume that hydrogen, the unit, was the one primordial substance of all the elements; or perhaps hydrogen and oxygen, since, so many of these numbers being directly divisible by four, a unit greater than one seemed to suggest itself. Here, then, was the genesis of a philosophic conception which has rendered Prout's name famous. Great was the excitement it caused. This resuscitation of the ancient idea of the essential oneness of matter appealed, as it still appeals, to the imagination of philosophers. Here, embodied and boldly enunciated, was a principle which many a chemist, more expert and so more cautious than Prout, had felt must underlie the mysteries of science; and, what was more important, here was a goal to the refining and super-refining of analytical procedure. On reading these papers, Thomson was led into the same train of thought as that induced by a criticism of his own table. He again pointed to the evidence contained there, and, in publishing

this table in a revised form, only allowed those values which were multiples of the atomic weight of hydrogen.

Between the years 1814 and 1818 Berzelius' attitude towards Dalton's hypothesis became more defined. He was dissatisfied with the "volume atom," whose magnitude could only be measured with certainty for hydrogen and oxygen. After all, it was the nature of the *atom* which was the goal of the chemist's research. It was only by a stretch of fancy that the idea of "volume atom" could have any meaning at all when applied to bodies in the solid or liquid state. The law of volumes, however, remained a momentous truth; it received its readiest explanation by assuming equal volumes of simple gases to be made up of equal numbers of "ultimate particles"—"particles," "atoms," "molecules," or "chemical equivalents," whatever one liked to call them—for then the values obtained for these particles, whether calculated from the measurement of gaseous volumes or from the results of ordinary chemical analysis, were identical. Berzelius, in reviewing the whole subject, became oppressed with the unscientific, slapdash manner in which it has been approached by his contemporaries. Was there no general principle, discoverable by a patient and acute study of the facts hitherto accumulated, which might guide one right in the choice of atomic weights from the many values submitted? Was there no means of knowing for certain whether a particular oxide had the formula RO , RO_2 , or R_2O , whether RO_2 or R_2O_3 ? After mature consideration, Berzelius could only answer in the negative. His atomic weights could at best only be regarded as probable, and in some cases hardly this, for that there was possibly an atomic ratio $2\text{R} : 3\text{O}$ was now to him something more than a lurking suspicion. Meanwhile he offers a revised table of atomic weights. The values given have in some cases undergone considerable modification in view of fresh and more accurate analyses, but the principles on which they are calculated remain the same.

Berzelius
discards
the volume
atom.

Any success which had hitherto marked Berzelius' efforts

to arrive at the true atomic weights was due to his adaptation of the law of volumes to Dalton's hypothesis, to his acceptance of this law as one based on the properties of matter in the last state of subdivision, in the state of atoms. He was limited in this as the number of elementary gases was limited. It was only when discovery of further generalizations as to the quantitative relations between matter atomic and matter in bulk had removed the scales from his eyes, that he could advance to place the atomic theory on an enduring pedestal. His corrected table of atomic weights was published in 1818. The year following brought with it the enunciation of two laws just of the character to supply the necessary data for a safe deduction of atomic ratios from the results of analysis; but the consideration of Dulong and Petit's law of atomic heats and Mitscherlich's law of isomorphism will aptly serve to introduce a new chapter. It only remains here to give a brief account of the accepted views (Berzelius') on the nature of chemical combination and the substances thereby produced.

Lavoisier's
doctrine
of fire.

With phlogiston discredited, it had become necessary to supply some new explanation, consistent with Lavoisier's doctrine, of the phenomena of flame. Lavoisier himself believed ignition due to the evolution as sensible heat of the heat latent in gaseous oxygen; and this, on first thoughts, seemed plausible enough, obvious cases being those of a metal calcifying in air and oxygen. Lavoisier's dictum ceased, however, to yield satisfaction as soon as attention was concentrated on the oxide of carbon, whose preparation involved the gasification of a solid element, and which was itself possessed of a higher specific heat than either of its components. The combination of hydrogen with oxygen was another case in point; moreover, it had been known for a considerable time that incandescence accompanied the union of certain metals with sulphur, solid substances all of them. Judging by experience, then, one would rather say that chemical combination, being accompanied by evolution of heat, often led, where the stronger affinities were concerned, to incandescence.

The inception of the idea of current electricity, and the striking results obtained through its employment by Berzelius and Hisinger on the one hand, and Davy on the other, focussed men's minds on this form of energy. As we have seen, it led to Davy's identifying chemical affinity with electricity. But it was Berzelius who developed this idea, demonstrated its concurrence with fact, and by its aid evolved a system which embraced the whole field of chemistry, animal, vegetable, and mineral, a system which withstood every attack for thirty years. Berzelius¹ started with the postulate that chemical affinity is in its nature electrical, that all chemical phenomena must therefore find explanation in terms of atoms furnished with preponderating polarity, either positive or negative. Now, whatever may be the nature of electricity, it is certain that it is never evoked in any substance other than in equal quantities of positive and negative, and so this fact of the preponderating polarity of a particular atom can only be explained on the analogy of a magnet with one pole weaker than the other. Two atoms, then, the one with preponderating negative, the other with preponderating positive polarity, combine with evolution of heat—it may be light, this is merely a question of degree—and a compound of the first order is formed. This compound will still be possessed of definite polarity, positive if it be potassium oxide, negative if sulphuric acid, and, when two such bodies come in contact, there will be a tendency to unite with partial neutralization of their charges, evolution of heat, and production of sulphate of potash. Even yet the positive polarity of the potassium oxide may assert itself, and the compound act accordingly; it may combine with sulphate of alumina to form a compound of the second order, the double sulphate of potash and alumina. And, again, the existence of potash alum with its water of crystallization shows that this double sulphate behaves as the electric antithesis of water in forming a compound of the third order, common alum.

Identity of
affinity
and elec-
tric attrac-
tion.
Berzelius'
theory.

If, then, chemical combination is dependent on the neutra-

¹ Berzelius, *Sur la Théorie des Proportions Chimiques*, p. 56. Paris, 1819.

lization of opposite electric charges in the concurrent atoms, decomposition must necessarily be associated with a redisposal of the neutral electricity, or a return to the combined atoms of their original polarity. Hence arise the phenomena observed on passing an electric current through a salt solution. Now, it is in solution that substances show themselves most active; and naturally, for only then are their ultimate particles absolutely free to oppose their different preponderating charges. Solution in itself is not to be associated with a play of chemical affinities, otherwise there would be no reason why all substances should not prove equally soluble.

Berzelius compiled a table comprising all the elements regarded from the electro-chemical standpoint. Oxygen, the most electro-negative, stood first, and potassium, the most electro-positive, last; while between these extremes were elements which, though acting as electro-positive to those above them, were electro-negative to those below. Still, one was not to regard this table as supplying the necessary order of affinities to oxygen. Sulphur, though standing higher in the scale, combined more strongly with oxygen than did lead, a fact readily explained by the reasonable assumption that the positive charge of the sulphur atom neutralized more negative electricity of the oxygen atom than the positive charge of the lead could do; though, relatively to each other, sulphur and lead were negative and positive respectively. Specific polarity, indeed, was to be differentiated from capacity for polarization, for though one could regard the first as constant for each atom, one could not so regard the second. The capacity for polarization seemed rather to vary with the temperature; certainly this was the case with carbon, whose affinities, or electric predilections, became so much more marked at a high temperature, and with gold, whose compounds under the same circumstances entirely lost their stability.

Berzelius' electro-chemical theory being accepted, all the observed laws of chemical combination followed as necessary consequences; even Berthollet's *Essai Chimique* was afforded a philosophical foundation: sulphuric acid reacts with copper

muriate, and there results copper sulphate and muriatic acid, for the negative electricity of the sulphuric acid neutralizes more positive electricity of the copper oxide than could that of the muriatic acid. But the muriatic acid atoms remaining in solution still retain their negative charges, whose cumulative influence, though each is weaker than that of the sulphuric acid atom, causes a limited redistribution of the atomic complexes in solution. Had, however, the initial change been associated with precipitation of the new substance or its elimination as gas from the sphere of action, such ultimate reciprocity would have been rendered impossible, and the change would have proceeded in one direction to completion.

Berzelius was responsible for a comprehensive theory of chemical reaction, a working system of notation, and a vast quantity of experimental data. Nor does the tale of his activity during the second decade of the nineteenth century end here, and no story of the chemistry of that time would be complete without some mention of the new nomenclature he was striving to introduce. It was Berzelius' belief that "precision and consequence in names contribute much to precision and consequence in ideas," that "confusion in the former will often cause confusion in the latter," and the demand for a new edition of the Swedish pharmacopeia gave him, in the year 1811, an admirable opportunity of putting this belief, as it affected his science, to the test of practice. Davy was of opinion that names given to various chemical substances should have a trivial nature, as otherwise every influx of new experimental data would necessitate complete change of the whole nomenclature, and so lead to confusion. With this attitude Berzelius had no sympathy; for him the terms applied must suggest place in a general system of chemistry, while they should be sufficiently elastic to allow for necessary increase of knowledge.

Berzelius
and
nomen-
clature.

As a basis for his terminology, Berzelius¹ chose Latin, the

¹ Cf. Berzelius, *Sur la Théorie des Proportions Chimiques*, p. 153 (also *Tables*). Paris, 1819.

one language common to all European nations. With the exceptions, therefore, of sulphur and phosphorus, the names of all his elements end in -um, thus—ferum, zincum, aluminium, magnesium. Those metallic oxides which show only a weak affinity in reaction, bodies with the formulæ $M + O$ or $2M + O$, were to be called suboxides; those which combine energetically with acids, simply oxides; and those which only combine after loss of oxygen, superoxides. He applied the term “acid” to such substances as the oxides of sulphur and nitrogen, which, on combination with metallic oxides, form salts. When one metal, say ferrum, formed two oxides possessing different degrees of “basification,” such names as oxidum ferrosus and oxidum ferricus would convey this knowledge; similarly the terms acidum phosphorosus, phosphoreus, and phosphoricus would imply different stages of oxidation of phosphorus. Salts produced by the reaction of the above two oxides of iron would have names made up of the terms ferrosus and ferricus on the one hand, and, where the acid in question was derived from phosphorus, of phosphis, phosphes, and phosphas on the other. Hence sprang such names as phosphis ferricus, sulphas ferrosus, murias hydrargyrosus.

Thomson's
system.

Berzelius regarded this system of nomenclature as superior to that advocated by Thomson in England. Thomson employed the prefixes prot-, deut-, tri-, and per- in differentiating between the several oxides of one element, and so left no room for any new oxide which might be discovered containing even less oxygen than the protoxide. Again, in naming such salts as those formed by combination of his protoxide and trioxide of iron with sulphuric acid proto- and per- sulphate respectively, he was inconsistently referring the different degrees of oxidation to the acid rather than to the base. As a matter of fact, both Berzelius' and Thomson's systems of nomenclature survive in terms which will at once suggest themselves to the reader.

CHAPTER VI

THE FORTUNES OF THE ATOMIC THEORY BETWEEN THE YEARS 1819 AND 1844

BERZELIUS' great genius is admirably exemplified by his consistent attitude towards the theory of Dalton³; he recognized the atom at once as a definite physical unit, whose magnitude could be determined by deductions from physical analogy alone. From the first he had clearly distinguished chemical equivalent and atomic weight, and his energies had been ever directed to finding some valid means of discovering their ratio. Dalton, Thomson, and the whole school of English chemists, while they too regarded the atom as a real physical entity, seemed unable to grasp what a determination of its magnitude must necessarily entail; and in a sense their attempts at solving the problem were of as little avail as those of Gay Lussac, Gmelin, and their followers, who, boldly declaring it insoluble, restricted themselves to a mere statement of experimental fact. In part it was mere lack of interest in physical problems, in part sheer lack of scientific perspicacity, which prevented the great bulk of Berzelius' contemporaries from grasping the latter's co-ordination of physical laws with Dalton's atoms. To an unprejudiced mind the evidence Berzelius offered for his new atomic values was overwhelming, yet when half the century was gone his very conception of atoms was almost forgotten.

Berzelius recognizes the necessity for physical data in determining atomic weights.

In the year 1819 Dulong and Petit published in the *Annales de Chimie et de Physique* an account of their investigation into the specific heats of various solid elements. The values obtained discovered a remarkable fact—they were inversely

The law of Dulong and Petit.

proportional to the atomic weights of the respective elements, or to submultiples of these weights. One had only to assume that some of the accepted atomic values were incorrect, as indeed was only too likely, considering the arbitrary character of the reasoning on which they were based, and here was revealed a great natural law—the atoms of all solid elements have the same capacity for heat. Dulong and Petit pointed to the following values among others as illustrating their law :—

	Specific heat	Atomic weight		Atomic heat
		O = 1	H = 1	
Bismuth	0·0288	13·30	106·4	0·3830
Lead	0·0293	12·95	103·60	0·3794
Gold	0·0298	12·43	99·44	0·3704
Silver	0·0557	6·75	54·00	0·3759
Iron	0·1100	3·392	27·136	0·3731
Sulphur	0·1880	2·011	16·083	0·3780

The constancy of the atomic heat was certainly only approximate, but the many sources of error to which determinations both of specific heat and atomic weight were liable rendered this not surprising. Dulong and Petit saw in the discovery a powerful auxiliary to the means of arriving at correct atomic weights: that multiple or submultiple of the experimental value or equivalent was to be accepted which, multiplied by the specific heat, gave a product 0·37 approximately.

Dulong and Petit received due honour on all sides as the discoverers of a very interesting and recondite physical truth; but the immediate practical results of this, as they affected the atomic theory, were small. Chemists were in no hurry to change many of their cherished atomic values to reconcile them with a principle of merely theoretic significance. This was markedly the attitude of Berzelius, as indeed one would expect. Berzelius' system of atomic weights had been drawn up after a most patient and open-minded examination of the facts; it was backed by the great law of volumes; and although he well enough understood that increasing knowledge might

demand considerable modifications, he also knew that increasing knowledge might prove Dulong and Petit's law to be not quite so general as its authors imagined. He would await further evidence. But before long a new body of facts accumulated, not more germane to the issue he had at heart than those just quoted, but of a character he was more ready to accept, and whose value none could so well appreciate. It was Mitscherlich's discovery of isomorphism which led to the new atomic weight table of 1826, a discovery which Berzelius regarded as the most valuable contribution to the science of chemistry since Dalton's discovery in 1803.

Though the phenomena of crystallization from solution must have been familiar to the observant from the very earliest times, it was long before any co-ordination was attempted between the form of a crystal and its composition. Even Boyle did not feel himself in a position to maintain that specific form was an inalienable characteristic of any particular salt; but with the beginning of a new century came more enlightened views, and conceptions of the crystalline form of a mass depending on that of its smallest particles bring us out of the atmosphere of vague wonder or mere speculation. We find the cube accepted as the ultimate form of the salt unit, the rhombic prism as that of the vitriols, while in 1707 Stahl bases his differentiation of soda from potash on the different form of their respective compounds. And so with the lapse of the eighteenth century there came belief in a relation between crystalline form and chemical composition, a belief that change in the one was dependent on change in the other. Processes of analysis were undergoing rapid improvement; mineralogy had become a science, and with it crystallography. On the one hand hundreds of minerals were passing through the skilled hands of Berzelius, Klaproth, and Vauquelin, while on the other crystallographers were proving that, whatever might be the crystalline character of any particular substance, the latter might be reduced by cleavage to one fundamental form; and, again, that the angles of all

Earlier views on the meaning of crystalline form.

crystals were constants independent of the nature and number of secondary faces.

Haüy's
classifica-
tion of
minerals.

In the year 1801, the Abbé Haüy produced a system of classification for minerals based first on their crystalline character, and secondly on their chemical composition; and his guiding principle was this, that every difference in the fundamental form of a crystal implied difference in its chemical composition. The immediate results of this classification were good. Minerals hitherto regarded as different he discovered to be identical, while at the same time he was led to differentiate between others confused by his predecessors and contemporaries. His deductions were often subsequently confirmed by analysis. But there was rapidly increasing a body of evidence which could not be readily reconciled with any such scheme as that of Haüy's. It was found that alums existed containing varying quantities of iron and yet retaining the customary octahedral form; that ammonia or soda might take the place of potash in these same salts without any corresponding crystallographic change; that minerals of the form of calcite existed containing many other bases besides lime; that carbonate of lime did indeed occur in two quite distinct crystalline forms; and that, finally, one might take mixed solutions of zinc sulphate and iron or copper sulphates and obtain from them crystals containing both salts, though ordinarily these occurred crystallized after quite different systems. Haüy would not deny his principle; substances crystallizing in the *regular* system, the alums, for example, might perhaps have different compositions; those calcite crystals which were found to contain carbonate of iron retained their customary form because the impurity was present, mechanically contained by the smallest particles of the mother crystal; and as to this mineral occurring crystallized after two essentially different systems, he was convinced that arragonite contained strontia; a crystal of copper sulphate crystallized out from a solution containing zinc sulphate in a form not its own because of the power of zinc sulphate to induce its own crystalline form in other salts. This assumption of predominant crystallizing power was widely

accepted, but otherwise Haüy found few adherents. The transparency of crystals was incompatible with mechanically contained particles; arragonite was found free from strontia. It was rather believed that the preservation of the gravimetric relation between base and acid was the ruling condition of identical form with varying composition, and that, as in the cases of barium, strontium, and lead sulphates, a common constituent might account for much.

It will be observed that the very difficult question of co-ordinating physical form with chemical composition had hitherto been attacked solely from the crystallographic side; yet it was a chemist who first grasped the truth and unified the whole mass of conflicting evidence by one all-embracing generalization. Eilhard Mitscherlich, in 1818, betook himself to Berlin, and there set to work on the salts of phosphoric and arsenic acids, that he might experimentally verify Berzelius' dictum as to the singular oxygen ratio between base and acid in these salts. Mitscherlich was only four and twenty years of age, and was quite ignorant of established opinion concerning crystallization; but he had made the acquaintance of the young mineralogist, Gustav Rose, from whose pen comes the following: "Mitscherlich told me of his work on the salts of phosphoric and arsenic acids, and how surprised he was to observe that the salts of both acids, so far as he could judge, had often the same form; and this though, according to his analysis, there was not the slightest trace of the one acid in the salts of the other. He asked me to measure the crystals. Even though Mitscherlich had not as yet busied himself with crystallography, he saw that this crystallization of differently composed bodies in the same form, if it could be established, would prove a fact of the highest importance; he was consequently impelled to busy himself more nearly with crystallography." Here we have the beginnings of an investigation that has become historic. An example¹ will serve to bring us nearer Mitscherlich at his task; it is the question of identity of the crystalline forms of the acid arsenates and phosphates of

Mitscherlich's law of isomorphism.

¹ *Ann. Chim. Phys.*, 19 (1821), p. 350.

potassium. First we find analyses to establish the equality of the ratios between the oxygen of base, water, and acid in either case :—

100 parts of arsenate contain—

63·87 parts of arsenic acid,

26·16 parts of potash,

9·97 parts of water,

the quantities of oxygen in the potash, water, and acid bearing the ratio 1 : 2·02 : 4·94.

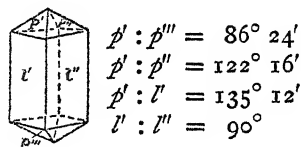
100 parts of phosphate contain—

52·26 parts of phosphoric acid,

34·56 parts of potash,

13·18 parts of water,

the quantities of oxygen in the potash, water, and acid bearing the ratio 1 : 2·11 : 5·11. And now comes the determination of the crystalline form and estimation of angles between different faces—



—with other measurements, all of which are found identical in the two cases.

Berzelius happened to visit Berlin in the summer of 1819, and, being made acquainted with the results of Mitscherlich's work, speedily made himself known to the promising youth. Hence it came that the autumn of the same year found Mitscherlich working in Berzelius' laboratory at Stockholm, and in December the first of his epoch-making papers was submitted to the Berlin Academy. As he had dealt with the acid phosphates and arsenates of potash, so he dealt with those of ammonia, and finds identity of crystalline form here also, identity too

with the crystalline form of the potash salts. He feels there is some guiding principle underlying this phenomenon, and seeks for another pair of acids which may help him to some generalization, but in vain. So he investigates the influence of analogous bases on the crystalline form of salts containing the same acid. The salts of barium, strontium, and lead have the same form, so have the sulphuric acid salts of various groups of metallic oxides, always provided the oxygen contents of base, acid, and water of crystallization preserve the same ratio in each group. The carbonic acid salts of chalk, zinc oxide, and the lower oxide of iron all occur as rhombohedra. Here was light! Conceptions of predominant crystallizing power might be relegated to the limbo of extinct philosophies; crystals of copper and zinc sulphate separate from a mixed solution in the same form, because both retain equal amounts of water of crystallization; and the same holds good for the whole class of alums, be they potash or ammonium salts. In fact, identity of crystalline character follows from similarity of composition. Here is Mitscherlich's proposition: "If two different substances combine with equal volumes of a third, the compounds so obtained on combining with another in all cases produce bodies of a similar structure; and when this third substance is the same, the bodies assume crystalline forms, whose identity as regards values of angles and numbers of sides is so complete that no difference can be detected even in these apparently so chance proportions." Those elements which conform to these conditions and produce salts, with the same acid or base, of similar crystalline form, he now includes in distinct classes, and for "convenience" sake adopts the term "isomorphism" suggested by Berzelius for the phenomena on which this classification depends.

Inductively Mitscherlich had arrived at his generalization; deductively he now proceeds to suggest crystalline forms for bodies whose practical investigation had not hitherto proved feasible. The sulphates of iron and zinc are obtainable in the same crystalline form, therefore their bases, the oxides of iron and zinc, must also be isomorphous. The minerals magnetite

Mitscherlich's deductions from his law.

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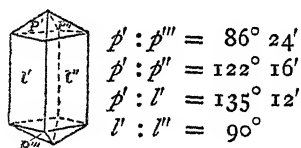
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and gahnite, compounds of the higher and lower oxides of iron, and of the oxides of aluminium and zinc respectively, are isomorphous; the lower oxides of iron being isomorphous with that of zinc, the higher must be isomorphous with that of aluminium.

On further investigation, however, Mitscherlich found that his dictum required modification. An examination of the crystals from solutions of the acid-soda salts of arsenic and phosphoric acids disclosed that these occurred in two forms, based on the rectangular octahedron and the right prism with rhombic base respectively. He had learnt meanwhile the facts relative to the crystalline forms of calcite and arragonite, and, regarding the oxide of calcium as composed of one atom of metal with two of oxygen, conceived that the different situations of these two atoms would account for the phenomena observed. In its amended form his doctrine was expressed as follows: "Equal numbers of atoms, when they are combined in the *same* manner, produce substances of identical crystalline form, which form depends, not on the nature of the atoms, but only on their number and mode of combination." And Mitscherlich's conception of dimorphism was ratified for elements also by his discovery of the two varieties of sulphur in 1823. The law of isomorphism quoted above reveals two facts, the first that Mitscherlich was an upholder of Berzelius' volume theory, the second that identity of crystalline form depends solely on the number of atomic volumes present in the compounds considered. From the year 1821 onwards he substituted the term atom for volume, while he soon convinced himself that the nature as well as number of combined atoms must be considered. Mitscherlich had adopted Berzelius' system of atomic weights, and had found in them an admirable explanation of his law; while, on the other hand, Berzelius gladly welcomed the law of isomorphism as vindicating the correctness of these weights, based somewhat insecurely, as they were, on so extended a view of the law of volumes and observance of mere chemical analogies. Neither felt any immediate call for change.

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But the demand for a new edition of his text-book caused Berzelius, in 1826, to reconsider his whole position. In reviewing his data he still maintained that his problem was definitely soluble in the case of those elements which are amenable to the law of volumes, hydrogen, oxygen, chlorine, and nitrogen, the last two of which he had now been brought to regard as elementary. For the rest one must rely principally on deductions from the progression in the oxygen contents of various series of oxides, on the relations between the oxygen contents of acid and base in salts, on the law of isomorphism as a means of generalizing from these facts, and finally, on the law of Dulong and Petit. Berzelius had discovered that in the neutral chromates there was three times as much oxygen in the acid as in the base, and this had suggested analogy with the neutral sulphates. If one writes SO^3 as the formula of sulphuric acid, one should obviously write CrO^3 as the formula of chromic acid. But since chromic¹ oxide contains only half as much oxygen as the acid, its formula must be written Cr^2O^3 , which implies the halving of the accepted atomic weight of the metal. (One must bear in mind that the isomorphism of the chromates and sulphates, and so the logical necessity for the change, was not observed till ten years later.) Now, chromic oxide is isomorphous with the oxides of aluminium and iron; therefore these too must have their formulæ changed to Al^2O^3 and Fe^2O^3 ; and if we write Fe^2O^3 for the higher oxide of iron, we must write FeO for the lower. Again, the lower oxide of iron is isomorphous with the oxides of zinc, magnesium, and calcium, whose formulæ must therefore also be simplified to ZnO , MgO , and CaO . So in general we must no longer regard active basic properties as indicating the presence of two oxygen atoms in the molecule, but rather as a sign of a constitution analogous to that of lime, whose formula is CaO . And under the influence of this train of thought Berzelius revised his atomic weights. A portion of his new table is reproduced here—

Berzelius
revises his
atomic
weights.

¹ *Jahresbericht*, 7, p. 70.

		O = 100	(O = 8)	
Hydrogen	..	6.24	(0.499)	} On the evidence of the law of volumes
Carbon	...	76.44	(6.11)	
Sulphur	..	201.2	(16.10)	
Nitrogen	...	88.52	(7.08)	
Chlorine	.	221.3	(17.70)	
Phosphorus	..	196.155	(15.7)	
Arsenic	...	470.042	(37.66)	
Tin	...	735.294	(117.839)	(SnO and SnO ²)
Chromium	...	351.8	(28.1)	(Cr ² O ³ and CrO ³)
Gold	...	1243.0	(99.4)	(AuO)
Silver	..	1351.6	(108.1)	(AgO)
Mercury	...	1265.8	(101.3)	(HgO and Hg ² O)
Iron	...	339.2	(27.1)	(Fe ² O ³ and FeO)
Calcium	...	256.0	(20.5)	(CaO)
Sodium	...	290.9	(23.3)	(NaO)
Silicon	...	277.468	(44.469)	(SiO ³ from its analogy with SO ³)

With the exceptions of silver and the alkali metals, the solid elements here conform to the law of Dulong and Petit, additional evidence which Berzelius laid stress upon for his justification. As to the exceptions, it was more probable that silver, sodium, and potassium should not be included in the generalization of Dulong and Petit than that the analogy between the oxides of these metals and other strong bases was purely superficial. Again, one observes that, with few exceptions, the atomic weights of Berzelius have assumed the general character of those favoured by the English and French schools of chemistry; but the reader must not forget that the tables of Thomson and Prout were merely the expression of an entirely unproven hypothesis, those of Gmelin and Gay Lussac the result of acknowledged empiricism, while eighty years of research have only served to strengthen the foundations of Berzelius' truly philosophic system.

First thoughts would suggest that nothing but good could flow from this identification of results; from henceforth there would be common theoretical ground for every school. It is very probable, however, that the younger generation, looking at results alone, and finding the great leaders of their science at one, confused identity of result with identity of theory, and

felt their *primâ facie* impressions established without further investigation. Moreover, as if to accelerate the coming confusion, Berzelius, in an evil hour, consented to a compromise, suggested doubtless by a desire for the unification of European chemistry, to which his new table so much contributed. The immediate occasion was this—the formulæ given by Berzelius to different substances were of the type PbO , FeO , ZnO , PbCl^2 , ZnCl^2 , H^2O , the corresponding formulæ of Gmelin and his school, PbO , FeO , ZnO , PbCl , FeCl , ZnCl , HO ; and Berzelius' unfortunate compromise was conveyed in his new formulæ $\text{Pb}\bar{\text{Cl}}$, $\text{Zn}\bar{\text{Cl}}$, $\text{Fe}\bar{\text{Cl}}$, $\text{H}\bar{\text{O}}$. This change he defended on the ground primarily that, having a standard of value in oxygen, "the centre round which all chemistry revolves," it seemed desirable to have means of simply expressing the combining unit of each element in terms of that standard; and, secondarily, that no one could say with certainty that nitrogen,¹ hydrogen, and oxygen ever did occur in combination otherwise than as double atoms. To this fact he gave expression in writing the formulæ for lead chloride and water $\text{Pb}\bar{\text{Cl}}$ and $\text{H}\bar{\text{O}}$, while at the same time he indicated by the symbols $\bar{\text{Cl}}$ and $\bar{\text{H}}$ those weights of chlorine and hydrogen which have the same combining value as the atom of oxygen.

Let us consider a moment longer the bearings, of this apparently trifling change on the subsequent history of our science. Here side by side are formulæ employed by those working in the spirit of Berzelius and others suggested by the conception of equivalents—

Ill effects
of the
barred
formulæ.

After Berzelius	After Gmelin
$\text{H}\bar{\text{O}}$	HO
$\text{H}\bar{\text{Cl}}$	HCl
$\text{N}\bar{\text{H}}^3$	NH_3
$\text{P}\bar{\text{O}}^5$	PO_5
$\text{Au}\bar{\text{Cl}}^3$	AuCl_3

For those ignorant or careless of the bar it was but a short step to the use of either system indifferently, and from this

¹ Cf. Blomstrand, *Chemie der Jäteszeit*, p. 12.

point one still shorter to the leaving out the bar altogether; and with the bar were likely to disappear the last traces of that philosophy which Berzelius had laboured so hard and successfully to establish. And in yet another direction¹ was progress impeded by this innovation; with the establishment of combination by equivalents all those investigations, which must necessarily have been suggested by Berzelius' old formulæ, as to the reason why hydrogen atoms combine in different numbers with other single atoms, were quashed. The nature of combination was no longer referred to atoms at all, but to units which might consist indifferently of one atom or two atoms or a certain number of parts by weight, and which were equivalent in the sense that a base and acid were equivalent, and hence could combine. No embryonic sense of a saturation capacity could survive this, and for many years yet chemistry was denied its most sensitive instrument.

Dumas discriminates between atoms and molecules. His vapour density apparatus.

In the *Annales de Chimie et de Physique*² for 1826, a young French chemist, Jean Baptiste Dumas, published an account of an apparatus he had invented for determining specific gravities, and of results he had obtained by its use. His thoughts had been led in the indicated direction by the general want of conviction as to the true relative weights of different atoms. Attributing this want to the various and often unsatisfactory methods by which the problem had been attacked, he decided that the only sure solution could come from a direct estimation of the weights desired, an estimation only possible after determining the specific gravities of the different elements and their compounds. Granted the truth of one postulate—that equal volumes of all fluids contain the same number of molecules—on which all men of science were agreed, his results were certain. One reservation, and that an important one, he made, however. The thought which had inspired Ampère's letter some twelve years before, and had been almost entirely unfruitful in the meanwhile, the thought that in speaking

¹ Cf. Blomstrand, *Chemie der Jetztzeit*, p. 24.

² *Ann. Chim. Phys.*, 33, p. 337.

of molecules we are speaking of physical, not necessarily chemical units, struck Dumas as essentially true, and as alone serving to explain the production of two volumes of steam from one volume of oxygen, and of two volumes of hydrochloric acid from one volume of chlorine or hydrogen. Since what holds good for oxygen, chlorine, and hydrogen might hold equally for all other elementary substances, the relative specific gravities of their vapours could suggest merely the relative weights of their molecules. How many atoms—elementary molecules he called them—these might individually contain he must remain ignorant. The specific gravities of readily volatile substances he measured by the method of Gay Lussac, and that he might extend his research to elements and compounds with high boiling-points he invented the apparatus which in its original form is still employed in our laboratories. And using this apparatus he discovered the specific gravity of iodine vapour to be 125.5 ($H = 1$), a number which, allowing for the greater possibility of minute accuracy in chemical analysis, was reconcilable with Berzelius' atomic value, 123.2. This was not at all the case, however, with the value 99.45 obtained for the specific gravity of mercury vapour, and consistency demanded that Berzelius' number 202.86, established though it was by all chemical analogy and the law of Dulong and Petit, should be halved, and the oxides of mercury formulated $2Hg + O$ and $Hg + O$ respectively.

Dumas now attempted to get at the relative weights of the phosphorus and arsenic atoms through a knowledge of the specific gravities of their hydrides and chlorides. To take an example:—the specific gravity of phosphorus chloride is 4.875 (air = 1); three volumes of chlorine condense to two volumes of this chloride, the volume of phosphorus vapour disappearing altogether. The analogy between the hydrides of nitrogen and phosphorus is strong, and it is likely, therefore, that, the former being composed of one volume of nitrogen and three volumes of hydrogen condensed to two volumes, the latter is composed of one volume of phosphorus vapour and three volumes of hydrogen, also condensed to two volumes, and

The atomic weights of phosphorus, arsenic, silicon and tin.

therefore that phosphorus chloride is composed of one volume of phosphorus and three volumes of chlorine condensed to two volumes. The weight of one volume of the chloride is 4.875, of two volumes 9.75. Let us subtract the weight of three volumes of chlorine, or 3×2.45 , and we obtain 2.3 as the weight of one volume of phosphorus, or 31.68 in terms of the hydrogen unit, a number agreeing well with the 31.34 of Berzelius. Similar reasoning brought him to regard 75.2 as the atomic weight of arsenic. The halogen compounds of silicon and tin he regarded as produced by the condensation of one volume of the radical and two volumes of the halogen to one volume, and, calculating the atomic weights of the elements on this assumption, he obtained the values 14.9 and 61.9 respectively^f.

Berzelius
refuses to
alter his
numbers.

Berzelius admitted this work to be of very great importance, though he considered the balance of evidence to be against altering his own atomic values to meet the views of the young French chemist. A case in point was that of mercury¹; undoubtedly the specific gravity of its vapour seemed to demand a halving of its atomic weight, but such a change as this would render necessary similar reductions in the atomic weights of many other elements, reductions which would be subversive of all the evidence available. And was it not odd that, while the specific gravity of liquid mercury was so much greater than that of solid iodine, in the state of gas this relation should be just the reverse? Then, again, in deducing the atomic weight of an element—say boron—from the specific gravity of its chloride, what right had Dumas to assume an analogy between its volumetric composition and that of ammonia, and, even if he had a right, was one to accept analogy for proof? Again, it was pure hypothesis to assume that one volume of silicon combined with two volumes of chlorine to form one volume of the chloride; all one knew was that two volumes of chlorine condensed to one volume of the chloride, and there was no greater certainty of the silicon vapour occupying one third of the volume of mixed gases than

¹ *Jahresbericht*, 1828, p. 67.

of its occupying one-fifth or one-seventh, in which case its atomic weight would appear very different from that suggested. And so Berzelius refused, and rightly, to submit to the dictation of Dumas' reasoning, and took up a tentative position, waiting for those more decisive experiments on the specific gravities of sulphur, arsenic, and phosphorus vapours which Dumas had promised.

Five years elapsed before an account of the new experiments¹ appeared. Meanwhile Dumas, though in this he stood alone, held to his opinion that 99.45 was the correct atomic weight of mercury, the arguments against this being based on an invalid analogy. His new experiments, however, showed that phosphorus, too, possesses an anomalous specific gravity, 4.32, corresponding to an atomic weight 62.2. Consistently with principle he now therefore wrote PCl_6 , PO_6 , PH_6 , as the formulæ for the quantities of the corresponding compounds present in one volume. So Berzelius was right in his strictures on the previous work, for here we have actually one volume of phosphorus vapour and six volumes of chlorine condensing to one volume. Dumas did not hesitate to cast aside the idea that ammonia and phosphoretted hydrogen were analogously constituted in view of the want of isomorphism between the phosphates and nitrates. The specific gravity of sulphur vapour was 6.51, and Dumas here found himself in a quandary. Already, in 1826, he had obtained this value, but since it did not coincide with that calculated from the specific gravity of sulphuretted hydrogen, he had refused to publish it. Was he to accept this value—93.74, in terms of hydrogen—as the atomic weight, neglecting the strongest evidence from chemical analogy, the law of isomorphism and the law of Dulong and Petit, or must he assume that at some temperature between the melting and boiling point of this element aggregation of the smallest particles had occurred, and that therefore the vapour consisted of molecules, themselves composed of three smaller molecules or atoms? He preferred the latter alternative, and suggested that this aggregation of particles might give an

Late researches of Dumas.

¹ *Ann. Chim. et Phys.*, 1832, p. 170.

explanation of the anomalous behaviour of liquid sulphur at 230°C .

Mitscherlich and the vapour density of arsenic and phosphorus.

Employing a modification of Dumas' apparatus, Mitscherlich,¹ in the year following (1833), succeeded in determining directly the specific gravity of arsenic vapour. The value referred to air was 10.6, which, assuming the vaporized molecules to consist of single atoms, would imply an atomic weight 152.64. But Mitscherlich was too clear-sighted to make this assumption. The molecule of sulphur, if we are to reconcile the evidence of its specific gravity with that drawn from its chemical and physical behaviour, must contain, as Dumas had suggested, three times as many atoms as the molecule of oxygen or other permanent gas; and on similar grounds the molecules of phosphorus and arsenic must contain twice as many. On the other hand, the number of atoms in the oxygen and mercury molecules must be in the ratio of 2 : 1.

Berzelius' criticism.

With this accumulation of fact, Berzelius'² attitude towards the question of the relationship between atomic weight and specific gravity was confirmed. There could be no question that the number of atoms present in equal volumes of the less volatile elements were not the same, and so determinations of their specific gravity could be of no assistance in fixing their atomic weights. Still, the relative weights of their vaporized molecules were of interest in that, as interpreted by his atomic weight table, they gave one a clue to the number of atoms present in each; they showed one, for instance, that the numbers of atoms present in the molecules of mercury, oxygen, phosphorus, and sulphur were in the ratio of 1 : 2 : 4 : 6. As he had stated before, there was no absolute method for the determination of atomic ratios; each accepted value must entail co-ordination of all the evidence known concerning the chemical and physical properties of the particular element considered.

Thomson upholds Prout's hypothesis.

Such of the English chemists as concerned themselves with the theory of atoms had not hitherto been very fortunate either

¹ *Pogg. Ann.*, 29, p. 193.

² *Jahresbericht*, 16, 31.

in understanding the problem set to them, or in submitting the conceptions they had to the test of laboratory experience. Thomson's great work, *An Attempt to Establish the First Principles of Chemistry by Experiment*, published in 1825, was of a character to draw from Berzelius the somewhat forcible remark¹ "the greatest politeness that can be shown the author is to regard the book as unpublished." The object of the book was to show that Prout's hypothesis as to the genesis of atoms was universally true; for Thomson had discovered that the atomic weights were all whole multiples of the weight of hydrogen, notwithstanding that Berzelius' indefatigable labours had shown just the contrary.

In the fifth edition of Dr. Turner's *Chemistry*, a standard text-book of the time (1833), the atomic² theory is very summarily dealt with: "In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent." The term atom has an historic interest for him as serving to keep green the memory of Dalton's ingenious speculation, but, with Davy and Wollaston, he would warn the reader against a possible confusion of the atoms of theory and the atomic or combining weights of practice, the foundations of the great chemical laws. Yet he knew the work of Berzelius and respected it, though he was a little annoyed by the latter's superfluous decimals, and he spoke of the inaccuracy of Thomson's views as judged by the most accurate analyses. It is pleasing to find that in compiling his volume Turner slowly convinced himself of the suitability of formulæ as a means to the exact conveyance of thought; though true, it was almost twenty years since the proposal for their employment had been made and acted on by Berzelius.

Turner
and
atomic
theory.

But a discovery of very real importance was Faraday's law of electrochemical action.³ Faraday had set himself to discover the necessary conditions of decomposition under the

Faraday's
law of
electro-
chemical
action.

¹ *Jahresbericht*, 1827, p. 78. ² Turner's *Chemistry*, pp. 195-199.

³ *Phil. Trans.*, 1834, p. 77.

influence of the electric current; he had found the need for some reliable standard by which to measure current electricity, and after demonstrating that the amount of hydrogen and oxygen evolved from water was unaffected by the size of the electrodes, the height of potential, the amount or character of the salts dissolved, or other variable characteristic, he initiated the use of what is now known so well as the water electrometer. In discussing his experiments he made use of a number of new terms, whose exact meaning he was at pains to define; such were "electrode" (from *ἡλεκτρον* and *ὅδος*), "electrolyte," "anode," "kathode," and "ion." The decomposition which ensues on the passage of the current through suitable media may be of two kinds, primary and secondary, which must be carefully differentiated. The primary or electrolytic is the immediate result of the transference of electricity from one electrode to the other; the secondary or electrochemical is consequent on an ordinary chemical action between the products of the primary decomposition and the water or other media in the vicinity of the electrodes. The decomposition of water is of the first type; that of sodium chloride, where the sodium, the kathion, reacts with the water at the kathode, is of the second. Now Faraday's discovery was this: if the same current is passed successively through a number of different electrolytes, whose decomposition is electrolytic, the weight of kathion or anion liberated in each cell is proportional to its equivalent. This law Faraday regarded as a final demonstration of the identity of chemical affinity and electric attraction, and the facts of which it is the generalization he considered most important in deciding what values are to be taken as the chemical equivalents, proportional numbers, or atomic weights—terms to him synonymous. As a matter of fact, its bearing on the question of the relative weights of the atoms was slight, though the values which Faraday eventually accepted had one great merit; they were the first which had been uniformly chosen in accordance with one fixed principle; they were really equivalent, though not atomic, weights. Among others he suggested the following numbers, potassium 39.2, sodium 23.3, and silver 108.

During the sway of phlogiston the word was in all men's mouths, its meaning in no man's mind. Stahl himself was very reserved in giving it definition. Yet chemical science progressed during the phlogistic period, and because of phlogiston. So too it was with Dalton's atomic theory. This theory has been the soul of nineteenth-century chemistry, yet during the first fifty years of that century curiously few seemed to understand what the word they all continually employed must imply. Most were content with a compromise. The real atom of recognized physical proportions they would reserve for their philosophical musings; in their practical researches they would employ the equivalent weight, calling it, however, an atomic weight, or a something which might be construed as a minimum quantity. It is indeed Dalton the physicist alone we have to thank for the atomic theory, for Dalton the chemist was little more enlightened than his predecessors Wenzel and Richter. It was the physicist who performed the unique service of showing how his hypothesis explained the laws of chemical and multiple proportions, striving to direct men's minds to the practical issue of what had hitherto been regarded as a mere metaphysical speculation; it was the chemist who, ably seconded by Thomson, entirely concerned himself with determining weights which were obviously merely equivalent, though he called them atomic; it was the chemist who set the lead to the French school and to the Germans, who, after a period of scientific apathy, rapidly assimilated and profited by the now stereotyped scheme of equivalent weights. True, these so-called atomic weights, equivalents, proportional numbers, mixing weights, did do service in that they helped to stamp chemistry with the impress of an exact science, but they had little bearing on a real theory of atomic constitution.

Conclu-
sion.

There was but one man, Berzelius, who by his work and writings showed that he had thoroughly grasped the problem set the world by Dalton. From the moment he settled himself to the task he understood precisely what was wanted, saw he must have physical data to accomplish the measurement of a physical unit, and grasped the full meaning of these data when

they were offered him. There is little to say in favour of the weights accepted to-day that Berzelius could not have said seventy years ago. How unsympathetic was the ear to which he preached one may gather from Dumas'¹ lectures on chemical philosophy, published in 1837. The author regards the conception of atomic weights as lacking definition; equivalents he could understand and determine; but atoms—he would banish the word from the nomenclature. And in 1844 comes an echo from Germany—Liebig² is speaking:—

“The sole aim of a chemical notation is to express clearly and succinctly the composition of chemical compounds; it will be best to clear it of all hypothesis therefore, so as not to have a system amenable to every new proposition. The number of equivalents of all the component parts of a compound is unchangeable and determinable; the exact number of atoms which combine to form one such equivalent will never be known.”

¹ Cf. Kopp, *Entwicklung der Chemie*, p. 438.

² Liebig, *Chem. Briefe*, p. 68.

CHAPTER VII

DEVELOPMENT OF ORGANIC CHEMISTRY

WRITING in 1810, Gay Lussac and Thenard¹ gave, as a reason for the slow progress of animal and vegetable chemistry, the inadequacy of the methods of organic analysis. This was immediately true, and so valid as a piece of special pleading for the importance of the analyses they had to contribute; but as an ultimate cause it would have been truer philosophy to urge the absence of any cogent reason for such analysis. This only came with the diffusion of Proust's doctrine of constant proportions, with all its suggestiveness when interpreted in the sense of Dalton. The extraordinary development of organic chemistry during the nineteenth century is a wonderfully complete vindication of the predominant position which the deductive method must hold in the laboratory. For generations previous to Dalton chemists, as industrious and as subtly-minded as have ever been, had endeavoured in vain to conceive the problem of organic chemistry, and so a mode of attack. For the subject-matter of their research was very different from mineral substance, so simply compounded, so stable, and often of such a beautiful crystalline character as to convey at once the sense of inherent purity and unity. Organic matter, though it was composed of comparatively few elements, and separable into units of quite few and limited classes, was so liable to immediate change, particularly in the presence of reagents, the instruments of diagnosis, that real knowledge of its units ever escaped the grasp. Moreover, a belief that the production of an organic body was subject to the necessary

Dalton's theory of atoms supplied the rationale of organic chemistry.

¹ *Recherches physico-chimiques*, ii. p. 265.

intervention of a so-called vital force, an *a priori* reason therefore against the possibility of its artificial synthesis, must have prejudiced the most patient research. But with the gradual permeation of Dalton's theory that all properties of matter were to be read in terms of atoms, equivalents, proportion numbers, mixing weights—it matters not what they were called, they all conveyed the root idea—hesitation vanished. Organic bodies, slippery though they were, being composed of atoms united in accordance with some knowable specific character, were proper subjects for attack, and for attack through the medium of analysis. In the light of this new hypothesis, the broader-minded saw that a differentiation of organic and inorganic bodies could have no valid foundation in fact long before experiment had bludgeoned this truth into the many.

State of
organic
chemistry
during the
last decade
of the
eighteenth
century.

Let the reader now, having conveniently rid his mind of all knowledge of organic chemistry in the modern sense, try to refurnish it with that of a well-informed and thoughtful student living in the last decade of the eighteenth century.

Lemery, in 1675, classified all substances as mineral, animal, and vegetable, and this system is yet retained in the text-books, though much of its former spirit is lost. It is now rather with a view to aiding the memory to hold firmly the ever-accumulating mass of facts, than of accentuating any radical difference between animal and vegetable bodies, that they, together with the products of their metabolism, are treated of as belonging to different types. Indeed, Macquer and Bergman have arrived at a division of all substances into the organic and the mineral; Berthollet and Proust, too, relegate vegetable and animal substances as containing carbon, hydrogen, oxygen, and sometimes nitrogen, to one and the same class, for which innovation the discovery of benzoic acid in the urine of cows, and the many points of identity between the animal and vegetable fats, give experimental foundation. Organic bodies¹ are those offered us as the seat of, or products

¹ Gren, *Grundriss der Chemie*, vol. i. p. 279.

of, vital force; they seldom occur except as complexes, from which immediate constituents can only be separated by such physical processes as solution, distillation, filtration, which incur no accompanying chemical change. Such immediate constituents are mucus, sugar, starch, glue, albumen, tartar; tartaric, oleic, benzoic, and similar acids; gum, fatty and ethereal oils, camphor, bitter and narcotic bodies—these specifically vegetable; fats, gelatine, cellulose, bone material, milk sugar, formic acid, carbonate of lime, and odorous bodies—these specifically animal. Such in the absence of any proof of impurity may be taken as the units of organic chemistry. The question as to their ultimate composition has become acute since Lavoisier's antiphlogistic doctrine has shown that such a conception as Macquer's, of an organic body containing phlogiston combined with an oil, can have no meaning. Though, long prior to Lavoisier, Van Helmont and Black pointed out that fixed air was produced on the combustion of an organic body, while Glauber, Scheele, and others noticed the simultaneous evolution of water vapour, it is only within the last twenty years that one has been able therefore to postulate the presence of carbon and hydrogen in the substances burnt. Now, since substances like wood, when destructively distilled in a vessel closed to the air, produce carbonic acid, we have evidence that they must contain oxygen also. Sometimes, as when tobacco or animal matter is distilled, there is an evolution of ammonia, clearly due to their containing nitrogen. But it is not always necessary to resort to such heroic measures as destructive distillation. Gallic acid or sugar, when treated with nitric acid, leave crystals of oxalic acid, and oxalic acid contains carbon, hydrogen, and oxygen; so too must the parent substances. After distillation of vegetable matter there often remains a residue, consisting partly of the alkaline carbonates, partly of chlorides and sulphates, or it may be of silica and alumina. These compounds are probably formed, by the union of the elements composing them, at the moment of disruption of the substance examined, though Vauquelin regards the carbonates certainly as pre-existent in

the plant. If alkaline earth or iron is discovered in the residue, it may be taken as a chance associate disconnected with essential composition. A general survey of the results of qualitative examination seems to suggest the presence of carbon, hydrogen, and oxygen as essential to the composition of an organic compound, these occasionally in conjunction with nitrogen, phosphorus, and sulphur, particularly in the case of bodies with an animal origin. As yet there is very little information published on the means of arriving at the quantitative estimation of these organic elements, which can scarcely be wondered at, for it is but a short time since Lavoisier's demonstration of the conservation of matter during chemical reaction, of that principle which alone gives meaning to a quantitative analysis. However, Lavoisier¹ has not only given us the principle, but examples also of its application in meeting the question of composition. With the greatest care he has ascertained that by igniting 28 parts of carbon in oxygen 100 parts of carbonic acid are produced; that on burning hydrogen in oxygen 15 parts of the former combine with 85 parts of the latter; and he has utilized this information in deducing the composition of oil, 100 parts of which burn out completely in 321 parts of oxygen with evolution of 140 parts of water and 281 parts of carbonic acid. He finds, in fact, that the 100 parts of oil contain 79 parts of carbon and 21 parts of hydrogen. Lavoisier goes even further. After a preliminary estimation of the composition of alcohol, he turns his hand to sugar, with results that he expresses in the form of the equation—

3 ozs. 7 gros of water + 2 lbs. 8 ozs. sugar produce, on fermentation,
 1 lb. 7 ozs. 5 gros 18 grains of alcohol + 1 lb. of carbonic acid.

"In this equation," says he, "there is only sugar whose constitutional parts are unknown to me. I know the composition of water, of alcohol, and of carbonic acid, and nothing

¹ Hoefer, *Histoire de la Chimie*, ii. p. 526.






is easier than to substitute these values in the equation established, and then deduce the constituent parts of sugar." Again, though we have no published account of the work, Lavoisier¹ has instituted the method of burning the less volatile bodies with mercury oxide, manganese oxide, or chlorate of potash, collecting and weighing the water and carbonic acid formed, and calculating from these data the weights of carbon and hydrogen present. The weight of oxygen in the agent of combustion being known, also that left after completion of the burning, he can discover the oxygen content of the organic body by the method of difference. Here are but the beginnings of an organic chemistry, and in the absence of any body of well-fortified numerical data it must be that we are almost entirely without knowledge of the internal structure of organic compounds, for, their constituent elements being so often the same, any differences between such compounds must in great measure depend on the quantities of these elements, and not on their number or nature. To Scheele's great work on the organic acids we owe much more than appears at first sight. The many acids he prepared, all undoubtedly distinct, yet composed of the same elements and complying with the canons of purity authorized by a knowledge of mineral compounds, suggest the possibility of separating many other so-called immediate principles into members of other equally well-defined classes of compounds. But for this we must wait. Meanwhile Lavoisier's view may be taken as established, that just as a simple substance combining with oxygen produces an oxide or acid, so a radical composed of two or more elements may similarly combine with oxygen to form an organic oxide or acid. Thus sugar may be taken as the lower oxide of such a radical, oxalic acid as the higher, and we have experimental evidence of this in the conversion of the one into the other on the addition of nitric acid. It will be the radicals, the organic elements, which undergo that quantitative change in composition associable with the different properties of the various acids. In view of our object

¹ Kopp, *Entwicklung der Chemie*, p. 524.

of metaphorically getting inside the organic units, such facts as the invariable elimination of "fatty acid"—a body very similar to acetic acid—on distillation of fats and fatty oils, the combination of the latter with the alkalis and alkaline earths to form soaps, the generic property which the ethereal oils possess of distilling unchanged, are not without significance. And since these oils constantly retain their smell, often of a very varying character, it seems we must give up our time-honoured notion of "aroma" being the one specific odorous principle of all matter. Finally, we cannot lay too much stress on the method of proof by synthesis; our feeling of certainty as to the nature of tarter and salt of sorrel is greatly enhanced by finding them identical with the salts produced by adding potash to tartaric and oxalic acids.

Dalton's
analyses
of organic
substances.

When expounding his atomic doctrine to the Manchester Philosophic Society in 1803, John Dalton made reference to what he regarded as the atomic weights of the two hydrocarbons, marsh gas and olefiant gas. An examination of his values made it clear that, relatively to the same weight of carbon, the one contained twice as much hydrogen as the other, a fact which he verified experimentally the year following by exploding the gases with oxygen. He then proceeded to apply this same method to the analysis of such readily vaporizable substances as alcohol and ether. The atomic weights of compounds being, in terms of his theory, the sum of the atomic weights of their constituent elements, and these being expressible by symbols, he was soon able to offer the following graphic presentments¹ of composition:—

Olefiant gas	
Marsh gas	
Alcohol	
Ether	
Sugar	

¹ Cf. *New View of Dalton's Atomic Theory*, pp. 45, 46.

a daring speculation, but one containing the germ of all later progress.

It was not in England, however, where scientific attention was concentrated on the broader aspects of Dalton's doctrine or on the confirmation of new elements, that the infant science was to be nourished, nor in Germany, given up to metaphysical speculation decrying the laboratory, but in France, where scientific activity was at its zenith; in Sweden, where lived Berzelius. Working on broader lines than Dalton, de Saussure, in 1807, attacked the less promising organic material, heated it out of contact with air, weighed the carbon left behind and the water collected, submitted any gas evolved to eudiometric analysis, and from the data so attained arrived at a composition; similarly, too, Berthollet in 1810.

De Saussure's and Berthollet's method of analysis.

Dissatisfied, however, with this rather slap-dash proceeding, Gay Lussac and Thenard were meanwhile evolving a process which was to place organic chemistry on a new footing, based on the only secure foundation, accurate knowledge of ultimate composition.

. Joseph Louis Gay Lussac was born in 1778 at St. Leonard, in the department of Haute Vienne. His father was a judge, and intended that the boy should practise at the bar; at the age of sixteen, however, he sent him to Paris to prepare for the Polytechnic school. Young Gay Lussac was not long in showing his extraordinary parts, and six years later was picked out by Berthollet to assist in his researches. Berthollet was a kindly master, and Gay Lussac's interests were wide. His analyses seldom confirmed the "essai statique," but Berthollet became his friend. He investigated the physics of gases, he marked the relation between their volume and temperature, bringing to the public ear a forgotten word of the Citizen Charles, and was made Fourcroy's demonstrator. In 1804 he made alone a balloon ascent, reached an elevation of 20,000 feet, observed atmospheric phenomena at high altitudes, collected samples of air, and on his return submitted these to eudiometric analysis in connection with Humboldt.

Gay Lussac, 1778-1850.

Hence he was brought later to his famous law of volumes. Gay Lussac was elected to the Academy in 1806. After some years as professor of chemistry at the Polytechnic School he was elected to the chair of physics at the Sorbonne in 1808, and in 1832 was translated to the professorship of chemistry at the Jardin des Plantes. He had meanwhile entered the Chamber of Deputies as member for his native province, and in 1839 was made a peer of France. He died in 1850. "Gay Lussac¹ was reticent, patient, persevering, accurate to punctiliousness, perhaps a little cold and reserved, and not unaware of his great ability. But he was also bold and energetic, not only in his work, but equally so in defence and support of his friends. The endurance he exhibited under the laboratory accidents which befel him show the power of will with which he could face the prospect of becoming blind and useless for the prosecution of the science which was his very life."

Gay Lussac it was who introduced our modern methods of acidimetry, and estimation of silver with standard salt solution.

Thenard,
1777-
1857.

When speaking of Gay Lussac another name instinctively springs to the lips, the name of Louis Jacques Thenard. Thenard was a native of Louptière in Champagne. He was born in 1777. His circumstances were narrow, but his parents were just able to provide him means to go to Paris and live there with a view to studying pharmacy. The youth was then sixteen years old; he attended the lectures of Fourcroy and Vauquelin, and persuaded the latter to take him as laboratory boy, that he might help with experiments without paying the to him impossible fee of twenty francs per month. Thenard improved every opportunity, found favour with his master, and was finally permitted to lecture in Vauquelin's absence. In 1798 he obtained a post at the Polytechnic School, and six years later, on the resignation of Vauquelin, was elected to the professorship of chemistry at the College of France. In 1810 he succeeded Fourcroy at the Polytechnic School, and the same year was admitted to the Academy.

¹ Ferguson, *Encyc. Brit.*, vol. 10, p. 124.

Thenard was raised to the peerage in 1832, and died in 1857. Like Gay Lussac, he was a member of that wonderful "Société d'Arcueil" which Berthollet had gathered round him. The Society continued from 1807-1817, and its published proceedings are a treasure-house of science. "Thenard¹ was tall and strongly built, his hair was thick and black, his eyes bright, and his manner active and prompt. He was above all things a teacher. His lecture experiments were few, well chosen, and accurately performed. If any failure occurred he would roundly scold his assistant, often apologizing for his vehemence when the short fit of anger was over. His lecture room, seated for 1000, was almost always crowded by eager and attentive students and visitors."

In the *Recherches physico-chimiques*² of Gay Lussac and Thenard, which appeared in 1811, we find an exhaustive account of their new method of organic analysis. The organic matter was finely powdered, also some fused chlorate of potash; weighed quantities of these, after being well dried in a steam-bath, were mixed, more of the chlorate being taken than sufficed to burn completely the organic body. This mixture was then moistened, worked to a paste, and this then squeezed into small pellets, a number of which, after dehydration in the steam-bath, were placed in a tube and then dropped one by one into the heated upright combustion-vessel till all the contained air had been driven out by the gases evolved. The tube containing the pellets was then weighed, the delivery tube from the combustion-vessel led under the collecting-jar containing mercury, and the analysis begun. Pellets were dropped into the chamber till the collecting jar was full, and the tube containing the surplus was weighed again. This operation was repeated three times, the weight of the pellets used being in each case the same, and the contents of the jars identical. To the gas in one jar a known volume of hydrogen was added that by explosion any hydrocarbon formed

*Recher-
ches of
Gay Lus-
sac and
Thenard.*

¹ Crum Brown, *Encyc. Brit.*, vol. 23, p. 252.

² ii. p. 265.

might be discovered and estimated. The carbonic acid was then absorbed, and the oxygen remaining, with any nitrogen, estimated. Any oxygen unaccounted for might be taken as having combined with hydrogen to form water. Here is an analysis of sugar which in the opinion of the authors was equal in accuracy to the best mineral analyses known :—

32 grms. of sugar on calcination left	...	0·045	gram. of ash.
Allowing for this correction, the sugar used weighed	0·300	gram.
The oxygen in the chlorate added weighed	...	0·627	gram.
The oxygen in the carbonic acid obtained weighed	0·322	} 0·625 gram.
And what remained in the collecting jar weighed	0·303	

There was, therefore, 0·1274 gram. of carbon present in the sugar, and since none of the oxygen of the chlorate was demanded for the hydrogen, it was to be assumed that the hydrogen and oxygen of the sugar were present in just the proportions to form water.* Gay Lussac and Thenard found therefore as the composition of sugar—

Carbon	= 42·47
Oxygen	= 50·63
Hydrogen	= 6·90

Similar analyses of gum arabic, starch, milk sugar, oak and beech wood revealed this astonishing fact, that however the composition varied, the hydrogen and oxygen were always present in just those proportions which on combination would form water. They then proceeded to establish the composition of a number of acids—mucic, oxalic, tartaric, and acetic—and, as before, considered the hydrogen and oxygen contents in relation to the composition of water. It was always with the same result; more oxygen was found than sufficed for the complete saturation of the hydrogen, though the excess differed in each case. Next, there followed analyses of various resins, wax, and oil of olives, and here it was the hydrogen which exceeded. The results of their work were so striking that

the authors felt themselves secure in making the following generalizations :—

1. A vegetable substance is always acid when it contains more oxygen than will form water with the hydrogen.

2. It will be always resinous, oily, or alcoholic when it contains less oxygen than suffices the hydrogen.

3. The body will be neither acid nor resinous, but analogous to sugar or ligneous fibre, when the oxygen and hydrogen are present in just the proportions to form water.

Analyses of such animal matters as fibrin, albumen, casein, and gelatine gave results similar in character, though here the question was complicated by the presence of nitrogen. This element was determined as gas, particular care being taken that no more chlorate was present in the combustible mixture than sufficed for the oxidation of the hydrogen and carbon. If, again, the hydrogen and oxygen were calculated as water, the excess of hydrogen and nitrogen deviated little from the quantities which would combine to form ammonia, and it seemed likely that a classification of animal matter analogous to that which obtained for vegetable might soon be established. But Gay Lussac and Thenard did not maintain that vegetable substances were really composed of carbon and water as such, or animal bodies of these with ammonia; it was quite too early for this. Their mode of calculation was, however, suggestive, and quite consistent with such significant facts as the easy resolution of sugar into carbon and water, and the ready evolution of ammonia from animal substance.

Many of the substances analyzed by Gay Lussac and Thenard might well have been accepted as single and pure; on the other hand, so much could hardly be said of beech wood or oak, wax or olive oil. So it was necessary that some guarantee of unity of substance should be found before the engine of ultimate analysis could work with maximum efficiency, and it was Chevreul's laborious and brilliant investigation of the fats which in large measure provided this. "The special philosophy of organic chemistry is almost entirely bound up in the

Chevreul's
classification
of
organic
substance.

circumscription of species." Thus wrote Chevreul¹ in 1824, thirteen years after the commencement of this memorable research. He had found that all organic substances fell into one of the following classes :—

1. Those from which one cannot separate several kinds of matter without materially altering its character ; such he termed *immediate principles*.

2. Bodies composed of two or more such immediate principles combined in a definite proportion.

3. Bodies made up of two or more of these principles combined in indefinite proportions.

It was only substances which belonged to the first or second class which could be regarded as species.

Chevreul's
work on
the fats.

Hitherto, prior to 1813, fatty bodies had been subdivided² into oils, butters, greases, fats, and waxes. Urged by the idea that nevertheless these same butters and waxes might include many substances differentiated by fusibility, odour, and colour, Chevreul proceeded to investigate their products of saponification. In the majority of cases he obtained glycerine and the potash salts of two acids, the latter usually distinguished by their melting-points. Cetine, however, gave no glycerine, but instead the substance ethal, while some of the waxes remained entirely unaffected. Was he, then, to regard the two acids with glycerine as immediate components of the unsaponified fat, and again, was he to rank this compound substance with species? To answer these questions Chevreul submitted the unsaponified fat to immediate analysis ; he digested it with cold alcohol, and so obtained two new fatty substances of different melting-points, which yielded, on saponification, glycerine and the solid and liquid acid respectively. Other fatty bodies behaved similarly, though yielding the two acids in very different proportions. Glycerine and acid were not then the immediate components of fats, and fats generically were not species. There was so a further question: were the fatty bodies separated by alcohol species? Fractional solution, a

¹ *L'Analyse Organique*, p. xi.

² Chevreul, *Recherches sur les Corps Gras*, p. 391.

process demanding our recognition, gave the answer; the fractions, successively yielded to the same quantity of alcohol, were identical. These new fatty bodies were then, indeed, species, but whether, being species, they were immediate principles themselves, or compounded of these, was uncertain. Analysis gave the following :—

	Stearin ¹	Olein
Glycerine	8.5	9.8
Margaric acid, M.P. 55° ..	80.0	22.08
Oleic acid	16.4	73.92

Might one not presume that *pure* stearin and *pure* olein would yield glycerine and margaric acid alone, or glycerine and oleic acid, that the fats in question were virtually immediate principles?

Whatever conception one formed of the internal structure of the vegetable and nitric ethers would cover equally that of the fatty saponifiable bodies, for both classes behaved quite analogously under the action of alkalis, or of air and heat, glycerine and alcohol with acids being respectively produced in the one case, acids in the other. Two explanations equally met these facts, and both were backed by respectable authority :—

Explanation of the behaviour of fats and ethereal oils with alkalis.

1. The presence of alkali determined acidity in a portion of the fat or ethereal oil, while the remainder, after fixing water, was separated as glycerine or alcohol. Here would be a case of the predisposing affinity of Fourcroy and Vauquelin, who could only by this conception explain the preparation of ether from alcohol or of carbon from sugar by the action of sulphuric acid.

2. The fatty substance or ethereal oil was of the salt type, formed therefore of an anhydrous acid, fixed or volatile, and anhydrous glycerine or alcohol. Saponification would then consist in these latter taking up water and separating as

¹ *L'Analyse Organique*, p. 129.

glycerine or alcohol while the alkali took their place. This would satisfy Berzelius' most fertile idea of the essential dualism of salts.

Many new acids discovered by Chevreul.

Chevreul's work resulted in the isolation of margaric, oleic, stearic, butyric, caproic, and capric acids; its fertility reminds one of Scheele, whose research, scarcely more brilliant, though more widely known, had discovered the first safe resting-place in the analysis of vegetable substance. What Gay Lussac and Thenard had done for ultimate analysis Chevreul had now done for immediate analysis, its necessary precursor, and all was ready for a general advance.

Berzelius would see if organic substance discovers the same laws as inorganic.

But we must go back a space, for, while Chevreul was striving with the vast and heterogeneous class of fatty substances, an even more important work was being slowly but surely carried to a conclusion. Berzelius, having demonstrated the conditions of combination in the inorganic world, was now concentrating his attention on organic substance. Did those few elements of which it seemed invariably made combine in accordance with established law, or did the mystery of vital force, life, find its correlate in a mystery of composition? Was, indeed, organic matter knowable to the chemist? Such were the questions Berzelius set himself to answer. What were the generalizations at which he had arrived after his long and laborious research into the composition of inorganic substances? They were these: there is never found here combination between three atoms of one element and four or five of another, but in every compound one of the elements exists in the state of a single atom. In any salt there always exists a simple relation between the number of oxygen atoms in base and acid. Now all evidence previously gathered pointed to the presence of at least three elements in organic substance, carbon, hydrogen, and oxygen, though sometimes there were more. Berzelius attacked the simplest compounds first, the vegetable acids,¹ bodies exhibiting the transition from inorganic to organic nature.

¹ *Annals of Philosophy*, 4, p. 330.

Mindful of Lavoisier's principles, he estimated the hydrogen from the water, the carbon from the carbonic acid, evolved on heating the substance with an oxidizing agent. He employed the lead salts, so readily prepared pure, mixing weighed quantities with brown lead oxide. This was in 1811, and, though the method was rough, the results were sufficiently momentous, for they proved—

- (1) that the water and lead oxide combined with the organic acid contained the same amount of oxygen ;
- (2) that there did exist a simple relation between the weights of oxygen in acid and base ;
- (3) that, read in the light of the atomic hypothesis, the analysis of oxalic acid would indicate the presence of 1 atom of hydrogen, 27 atoms of carbon, and 18 atoms of oxygen.

While some of the evidence, then, was in accord with his previous generalizations, the rest was in absolute contradiction. Was he to reject the atomic hypothesis, or revise his philosophy of composition ?

Meanwhile news was come of Gay Lussac and Thenard's¹ research. A modification of their analytical method was immediately adopted by Berzelius. For the upright chamber he substituted an almost horizontal tube, wrapped round with tinfoil, to prevent bulging, and containing successively a mixture of common salt and potassium chlorate, then this mixed with the salt to be analyzed, and, finally, more of the chlorate mixture. The tube was heated gradually along its length, and the evolved gas, after passing through a weighed calcium chloride tube, was collected over mercury, and its carbonic acid absorbed by sodium hydrate. Berzelius was still instant in his recommendation of the compounds with binary oxides for analysis ; he felt that so reliable a body as lead oxide would act as a break on the vagaries of organic composition. Let us take an example ; we shall thus best conceive Berzelius' problem and manner of attack. A preliminary analysis of lead

Berzelius
modifies
the method
of ultimate
analysis.

¹ *Annals of Philosophy*, 4, p. 404.

citrate, the lead being weighed as insoluble lead sulphate, gave the following:—

Citric acid	34·18	or	100
Oxide of lead	65·82	or	190

containing 13·588 parts of oxygen. A combustion taught him that 100 parts of the acid contained—

Hydrogen	3·800
Carbon	41·369
Oxygen	54·881

approximately four times 13·588, the oxygen content of the base. It might be taken, then, that citric acid contained at least 4 atoms of oxygen, 4 atoms of carbon, and 4 atoms of hydrogen, though there was no evidence that the formula for its lead salt was $\text{PbOC}_4\text{H}_4\text{O}_4$, rather than some multiple of this.

And in this manner Berzelius investigated the composition of many other well-known acids and substances of the sugar family. His results all pointed in the same direction. No analogy could be drawn between the laws of definite proportions obtaining in mineral substance and those governing the composition of organic matter. Yet, read by the light of the law of volumes or its corollary, the atomic theory, the quantities of different elements combined in the matter did exhibit a simple ratio. It was, indeed, the atomic theory alone which could enable one to understand properly the composition of organic substances. Their number was so vast, the elements they contained so few, and the percentage differences in composition so small, that one was lost till one could recognize that a single atom of oxygen differentiated citric from succinic acid, two atoms of carbon, succinic from acetic.

Hitherto (up to 1816) Berzelius had strongly urged that organic compounds¹ should be considered as inseparable, theoretically and practically, into nearer components; the

Berzelius' conclusions.

Berzelius regards organic matter dualistically.

¹ *Essai sur les Proportions Chimiques*, p. 44.

three, four, or five elements of their composition must be combined each with the other indifferently. But now his philosophic spirit demands unity over the whole of the chemist's domain. All vegetable substance contains oxygen; so let us take it that this forms the one nearer component which, combined with the other—a compound radical containing hydrogen and oxygen, produces it may be an acid like acetic, it may be a neutral substance like sugar. It may be assumed that the combination is induced by the two radicals retaining a negative and positive charge of electricity respectively. One must remember, however, that while some ternary oxides, like acetic, tartaric, and oxalic acids, will thus exhibit a negative polarity which rivals that of the most active binary oxides, others, like sugar, are almost neutral, facts which the mind refuses to reconcile. But this may be sheer ignorance, and therefore let us not lightly throw aside an idea which has already proved so fruitful in another sphere. May it not be, indeed, by reason of these very electric charges,¹ peculiarly modified as they must be, on the great number of elementary atoms which enter into the composition of the ternary and quaternary oxides, that these are in general so feebly active and so readily dissoluble into the stable bodies, water and carbonic acid?

The idea of a radical forming a proximate constituent of organic compounds did not originate with Berzelius, for it was in this sense that Lavoisier had spoken of sugar and oxalic acid as lower and higher oxides of the same hydrocarbon. It was not in this sense, however, that he had spoken of his difficulty in dissociating his conception of sugar from that of carbon combined with water, nor that Gay Lussac and Thenard had for the moment conceived their three great classes of organic compounds as differentiated by the hydrogen or oxygen contained in addition to carbon and water. Let us now, from the point of view of these philosophers, consider organic composition more intimately, remembering that there was nothing *a priori* unreasonable in regarding one compound as made up

Organic matter a composite of simple inorganic substances.

¹ *Annals of Philosophy*, 4, p. 329.

of others simpler but equally stable. There was no sense of saturation capacity referable to the elements; one only knew that elements combined, acids and bases combined, salts combined. De Saussure, in 1814, after confirming Dalton's analysis of olefiant gas, submitted ether and alcohol vapour also to explosion with oxygen. Gay Lussac, with the results of these experiments in his mind, considering that olefiant gas must have some special relation to alcohol, from which it is so readily prepared, familiarized too with the idea of reading composition in terms of complexes which analysis showed might be present, and urged by his faith in simple volume relations, was led to regard alcohol and ether as containing olefiant gas and water vapour combined in the volume ratio of 1 : 1 and 2 : 1 respectively. Here would certainly be valuable theoretical confirmation of de Saussure's analyses. Further evidence of the correctness of this view was offered by Robiquet and Colin, showing, in 1816, that the haloid ethers of alcohol must be regarded as combinations of this same olefiant gas with equal volumes of halogen acid, not of alcohol and acids, as Boullay had maintained. These general conceptions seemed fruitful, so Döbereiner¹ now wrote oxalic acid $\text{CO} + \text{CO}^2$, sugar $\text{CO}^2 + \text{CH}^2$, alcohol $\text{CO}^2 + 3\text{CH}^2$, and formic acid $\text{HO} + 2\text{CO}$; while Chevreul,² in 1824, boldly and without reservation accepted Gay Lussac and Thenard's classification of 1810.

Berzelius insists on his radicals.

But Berzelius³ had at once detected danger in this speciously reasonable method of expressing composition; the number of organic compounds was too great to allow of their composition being so expressed; moreover, there would then be an inducement to correct analyses to meet preconceived views, too alluring for fallible man. And with the application of his electro-chemical theory to organic matter his heart hardened still more, for with this theory such conceptions of composition were utterly incompatible. Radical and oxygen, such alone are

¹ Kopp, *Geschichte der Chemie*, iv. p. 319.

² *L'Analyse Organique*, p. 191.

³ *Essai sur les Proportions Chimiques*, p. 47.

the nearer components. De Saussure and others may speak of oils which contain carbon and hydrogen only, but let them repeat their analyses; it is more likely they have made a mistake than that one's whole idea of organic composition is erroneous.

Gay Lussac, in 1815, had shown that prussic acid, like hydrogen sulphide, was entirely free from oxygen; that it was a compound of hydrogen with a radical cyanogen; that the latter could be itself prepared and would combine directly with chlorine. One would think that here was a weapon which might have been used with telling effect by either Berzelius or his opponents. But if cyanogen was capable of a separate existence, its acid might be relegated to the bulk of inorganic compounds; its consideration was not here in point. It is of importance, historically, that copper oxide was used by Gay Lussac as oxidizing agent in the analyses of the cyanides; its general use was thenceforth established.

Gay Lussac and the cyanogen radical.

After Robiquet and Colin's demonstration of the composition of the haloid ethers, there prevailed a general impression that other long-known compound ethers contained as proximate components alcohol and the anhydrous acid, or, as Berzelius maintained in 1825, ether and the hydrated acid. Ether and alcohol Berzelius regarded as oxides of quite different radicals, and analysis had shown him that it was the first, and not the second, which was here combined. But in 1828 there was published a paper¹ in the joint name of Dumas and Boullay which shed great light on this question. Dumas and Boullay had begun an investigation of the compound ethers, convinced that the province of the mineral acid necessary to their preparation was the preliminary conversion of alcohol into ether; they were naturally aware how Chevreul had shown that fats might be regarded as formed of anhydrous fatty acid and a radical which, on saponification, combined with water to form glycerine. They had prepared a number of the compound ethers, determined their elementary composition by Gay Lussac's combustion method, their vapour density, and the

Dumas and Boullay's etherin theory.

¹ *Pogg. Ann.*, 12, p. 432.

acid and alcohol separated on saponification. The inference to be drawn from their experiments had been ever the same; compound ethers contain as nearer components ether and anhydrous acid. Thus expressed in volumes ($O = 8$, $H = \cdot 5$, $C = 6$) oxalic ether had the composition $C_6H_5O_2$, or some multiple of this—most probably $2C_6H_5O_2$, or $C_{12}H_{10}O_4$ —which suggested $C_{10}H_8O$ and C_4O_3 , ether and anhydrous oxalic acid, as nearer components; for the vapour density $6\cdot609$ calculated on this supposition would agree fairly with the $6\cdot081$ of practice. A further analysis confirmed Dumas and Boullay in their opinion. The oxalic acid was estimated as calcium oxalate, the alcohol by means of the hydrometer, a portion of the ether being distilled with potash. From 100 parts there were obtained—

$$\begin{array}{r} 48\cdot98 \text{ acid} \\ 62\cdot18 \text{ alcohol} \\ \hline 111\cdot16 \end{array}$$

whereas theory demanded $112\cdot24$.

Now Dumas and Boullay accepted Gay Lussac's opinion that ether and alcohol were the first and second hydrates of "hydrogène bicarboné"—they formulated them $4C_2H_2\cdot\dot{H}H$ and $4C_2H_2\cdot 2\dot{H}H$ respectively—and were therefore constrained to regard the compound ethers also as bodies containing this same radical $4C_2H_2$. So Chevreul had thought. There seemed here a family relationship closely analogous to that found among the ammonium compounds, and indeed the analogy between the compound ethers and ammonias went beyond mere formulation. If an ether was treated with ammonia, the latter took the place of part or all the hydrocarbon, without in any measure affecting the neutrality of the compound. If the hydrocarbon were only soluble in water, it might well be as alkaline as ammonia. The tendency to abjure water of crystallization seemed common to ethers and ammonium salts alike. And Dumas and Boullay gave point to their suggestions by drawing up the following table:—

	Salts of the "hydrogène bicarboné"	Ammonia salts
The chloride	$2C_2H_2.2HCl$	$2NH_3.2HCl$
The iodide	$2C_2H_2.2HI$	$2NH_3.2HI$
The nitrite	$4C_2H_2.N.N.HH$	$2NH_3.N.N.HH$
The acetate	$4C_2H_2.C_4H_6O_3.HH$	$2NH_3.C_4H_6O_3.HH$
The oxalate	$4C_2H_2.C_2O_3.HH$	$2NH_3.C_2O_3.HH$
Cane-sugar	$4C_2H_2.4C.HH$	
Grape-sugar	$4C_2H_2.4C.2HH$	

—a table which marks an advance that has rendered their investigation famous. Here at last were the beginnings of a classification philosophically sound and experimentally verifiable.

"Not even the compounds of the hydrocarbon with water are alkaline; nor do its salts react like those of ammonia. We know that ether does not combine with an anhydrous acid," wrote Berzelius in his yearly report.¹ "His (Dumas') idea of a carbonated alcohol and a carbonated ether in the sugar group may do for the French; it is certainly ingenious, possibly right as far as the quantities of the elements are concerned, but philosophical, no!"—this in a letter² to Wöhler.

Berzelius' criticism of the etherin theory.

There were few dogmas believed in more devoutly by Berzelius and the bulk of contemporary chemists than this, that difference in property could only be a consequence of difference in composition. The attitude was pernicious in so far as it tended to stifle any striving after wider information than was conveyed by a mere empirical formula. Facts were accumulating, however, which were irreconcilable with any such limitation. In 1822 Wöhler published an analysis of cyanic acid; it was at the outset of his career, and his position was yet to be established. Another young German, Liebig, had found an entrance to the laboratory of Gay Lussac, and was

Wöhler and Liebig analyze cyanic and fulminic acids, respectively with identical results.

¹ *Jahresbericht*, 1829, p. 296.

² Berzelius-Wöhler, *Briefwechsel*, I, p. 216.

there at work on the fulminates in collaboration with his famous preceptor. To the astonishment of both master and student, the fulminic acid was composed of the same elements, combined in the very same proportions, as was Wohler's cyanic acid. A case of identical composition with different constitution, said Gay Lussac. Absurd! rejoined Berzelius. Liebig then analyzed silver cyanate, and found that it contained 71 per cent. of the silver oxide, and not the 77.23 of Wöhler. The Parisian seemed to have the victory, and exulted in it. Wöhler¹ repeated his analysis, and found 77.5; Liebig had used impure material. Finally, in 1826, Liebig once more examined both the fulminate and cyanate, and found their composition identical. Even Berzelius seemed convinced.

Faraday
investi-
gates cer-
tain hydro-
carbons.

Meanwhile Faraday² in England had published a paper bearing on this same question of identical composition associated with different properties. In the receivers of the "portable gas" company there was always an oil deposited, and this oil Faraday had investigated. Having found a new carburet of hydrogen (benzene) in the liquid portion, he turned himself to the more volatile fraction which the condensed liquor evolved on being removed from the chamber. This fraction liquefied at 6° Fahr., and detonation with oxygen showed it to have the same composition as olefiant gas. But its vapour density was twice that of olefiant gas, and, moreover, though it combined volume for volume with chlorine, the body so formed contained twice as much carbon and hydrogen for the same amount of chlorine as chloric ether did. Mindful of the similarly anomalous results of Liebig and Wohler, Faraday thought that here again was a case of "different states of combination" of the same elements united in the same proportions.

Berzelius
and phos-
phoric
acid; he
accepts
isomerism.

The question raised by these investigations was still to many minds an open one; Berzelius certainly was unconvinced. But years ago, in 1816, Gay Lussac had noticed the curious behaviour of water towards potassium phosphate after

¹ Berzelius-Wöhler, *Briefwechsel*, I, p. 101.

² *Phil. Trans.*, 1825, p. 440.

fusion, and in 1825 Berzelius and Engelhart found that the hydrated acid itself acted with reagents very differently before and after fusion, though its quantitative composition remained the same. Berzelius was moved. But it was only in 1830, after he had finally assured himself that racemic acid, though behaving so differently, had the very same composition as tartaric acid, bore in fact the same relation towards it as fused to unfused phosphoric acid, that his doubts vanished. There did then exist bodies having the same composition yet exhibiting different properties, and such he would call "isomeric." But there was a radical difference between the isomerism of racemic and tartaric acids and that of Faraday's olefines; he would hence distinguish between "metameric" and "polymeric" compounds.

This same eventful decade was to see yet another time-honoured superstition removed. Gmelin, writing in 1817, had spoken of the differences between organic and mineral matter being more easily felt than defined; the impossibility of artificially preparing a member of the former class had appealed to him, however, as one certain differentia. "You may remember," writes Wohler¹ to Berzelius, in the February of 1828, "how while I was with you, when trying to make ammonia combine with cyanic acid, I always obtained a crystalline body which gave the reactions of neither one nor the other. I have just made this crystalline body the subject of a little investigation, preparing it by the action of ammonia on lead cyanate, and have discovered it to be nothing else than urea. This may be taken as an artificial production from inorganic substance." "A right weighty and pleasing discovery," returned the Sage, who, however, with others, had long foreseen its possibility.

Wohler prepares urea from ammonium cyanate.

Prout² has shown the formula for urea to be $C_2O_2N_4H_8$. "The composition of ammonium cyanate should be the same if we assume that in ammonium cyanate, as in all ammonium

Another case of isomerism.

¹ Berzelius-Wohler, *Brüfwechsel*, I, p. 206:

² *Pogg. Ann.*, 12, p. 250.

salts, an atom of water is taken up." Here would be excellent confirmation of Gay Lussac's and Faraday's opinions that difference of property is not incompatible with similarity of composition. "Does not the investigation show the insufficiency of the conception of alcohol as a compound of olefiant gas and water, or of hydrocarbon and carbonic acid?" And indeed there now seemed little security in judging from products of reaction to constitution of substance. Such were Wöhler's¹ comments.

¹ Berzelius-Wöhler, *Briefwechsel*, I, p. 207.

CHAPTER VIII

THE RADICAL THEORY AND DISCOVERY OF SUBSTITUTION

"THE history of a nation is the history of its greatest men." Can we say this of the history of a science also? Yes, and no; yes, for it is the generalizations of its greatest men from facts hitherto misunderstood or carelessly neglected that mark the advance,—the generalizations of a Boyle, a Lavoisier, a Dalton, or a Berzelius,—that, by defining the boundaries of our knowledge, make us sensible of new phenomena, the study of which allows of a new generalization, a further advance: and no, for the generalizations of the individual may be false or not entirely true; yet there is still progress, his personal error being eliminable under the fire of criticism, and there being nothing irretrievable in a momentary loss of truth, as there is in acts committed through a patriot's loss of self-command. Does, then, the inclusion of brief biographical appreciations in a work of this character require excuse; should a history of chemistry be devoted entirely to tracing the development of the science, read as a body of facts and theories co-ordinating these facts, with the personal equation ruled out? If one regards science objectively, such must be the case; if subjectively, as needs must be, no; one requires a teacher to expound the chemistry of seventy years back as much as to expound that of to-day, and the better one knows and appreciates the teacher, the more rapid the progress. Yet again, while one demands the how and wherefore of that body of fact and opinion which we to-day call chemistry, one also demands the how and wherefore of the

Has
biography
rightly
a place
in the
history of
chemistry?

means by which it has been accumulated. No one who has visited the German University towns can avoid being struck with the munificence with which science has been provided for, yet speaking of a period scarce eighty years gone Liebig could say, "it was then a wretched time for chemistry," for there was not one public laboratory in the country, nor a chemist efficient to direct, had it existed. Liebig had needs go to Paris and find admission to the private laboratory of Gay Lussac; his countryman Mitscherlich had already sought Berzelius at Stockholm, soon to be followed by Wohler and others. It was not pure chemistry, fact or hypothesis, that effected the extraordinary change in the conditions of work; it was rather pure personality, the personality of Liebig.

Liebig,
1803-
1873.

Justus Liebig¹ was born at Darmstadt in 1803. The fact of his father being a dealer in dye-stuffs brought him early into contact with laboratory problems. His spirit of enterprise and independence showed itself early. "I will be a chemist," said he, in answer to a reproachful question of his schoolmaster, and the very boys were overcome with laughter. At fifteen years he was sent to a neighbouring town to learn the business of apothecary. But pharmacy was not chemistry as Liebig was beginning to understand it, so he entered the University of Bonn. Here was certainly change, much "ingenious contemplation," but no chemistry. He travelled to Erlangen, where he heard lectures, read books, and at nineteen obtained a degree. Then his chance came. His ability being made known to the Grand Duke of Hesse Darmstadt, he was provided with the means of studying in Paris. There worked those giants Gay Lussac, Thenard, Chevreul, and Dulong; nor was it long before Liebig was received into the laboratory of Gay Lussac. Liebig had meanwhile won the appreciation of Humboldt; his was a personality that inspired immediate and warm friendships. "Of slender form was he, a friendly earnestness in his regular features, great brown eyes with shady eyebrows which attracted

¹ Shenstone, *Life of Liebig*, p. 80.

one instantly." It was Humboldt who, in 1824, brought him as extraordinary professor of chemistry to Giessen. Two years later he was elected to the ordinary professorship, which office he held for the next six and twenty years. The dull little town of Giessen became famous; the fires of Liebig's laboratory acted as a beacon light, attracting chastered spirits from the four quarters of the civilized world. For it was not long before the master had roused the Darmstadt Government to build a laboratory where all might come and seek and find. And the movement spread. Liebig, through his pupils, tintured the world; there were other governments than that of Darmstadt, and soon there were other public laboratories than that of Giessen. In 1845 Liebig was created Baron. In 1852 he accepted a call of the Bavarian Government to the Munich professorship of chemistry. Warmly appreciated by the Bavarian Court, entering into the social and philosophical life of the university town, courted by all the scientific circles of Europe, yet continually fighting weakening health, Liebig passed the remainder of his life in Munich. He died in 1873.

A warm-hearted, warm-tempered man was Liebig. He was essentially a pioneer, and a pioneer has to fight. His criticisms on what he conceived an error certainly did not err on the side of leniency, yet while men fought him they loved him. The last thirty years of his life were devoted to the elucidation of the principles which underlie correct agriculture and enlightened pharmacy. Great fights there were in the new arena, for here Liebig had to meet crass and boorish ignorance on the one hand, and subservient regard for precedent on the other. But he was successful. Is not mineral manure an indispensable asset of the successful cultivator of to-day? Who of us has not partaken of beef extract?

When a great worker for science dies, it is the happy lot of a chosen colleague to deliver an address in commemoration of what the lost one has achieved. When Liebig died there was found no one who sufficiently comprehended all the phases of his life's work to do this; three addresses were delivered, each by a master.

Wöhler,
1800-
1882.

While Liebig was working in Giessen, another young German, whose name has already been met more than once in these pages, was laying the foundations of a world-wide reputation. Three years older than Liebig, Friedrich Wöhler was born at Eschersheim near Frankfort in 1800. His father, an equerry to the Elector of Hesse and a man of means, sent him in his twentieth year to the University of Marburg to study medicine. But Wöhler had early been inspired with the love of pure science, and he soon left Marburg for Heidelberg, to sit at the feet of the famous Gmelin. Won over from medicine by his preceptor, he set off in 1823 for Stockholm, to be received into Berzelius' laboratory. A few months spent there, and he was back again in Germany, a teacher of chemistry in the Berlin trade school. This was in 1825. In 1831 he was appointed Professor of Chemistry at Cassel, where he remained nearly five years. Then he went to Göttingen, whose university he adorned for the next forty-six years, attracting to his laboratory and lectures thousands of students from all quarters. As a teacher he ranks with Berzelius and Liebig, perhaps higher than either, for Berzelius' laboratory was small, Liebig's interests were somewhat specialized. But whatever branch of chemical science was to be understood, the student had only to arrive at Göttingen and the goal was within reach. A happy temperament was Wöhler's; *mens sana in corpore sano* might well have been his epitaph. His fourscore and odd years of life brought him into contact with all the strifes that rage over the childhood, youth, and maturity of a new science, yet were his word and action ever for peace. Barely half his life was spent when the great Berzelius passed away—Berzelius, to whom, since his first visit to Stockholm, he was bound by ties of the warmest affection and veneration. Nine years did he outlive the fiery Liebig. Ever since, in 1828, these old antagonists had met, there had existed an ever-ripening friendship between them, and dear must have been the thought that to all time, by virtue of their joint work, the name of Liebig must recall that of Wöhler, the name of Wöhler that of Liebig.

In the *Annalen der Pharmacie*¹ for the year 1832 there was published a paper under the joint names of Liebig and Wöhler. This paper, entitled "Investigations into the Radical of Benzoic Acid," was the outcome of four weeks' strenuous labour in Liebig's laboratory at Giessen, where Wohler, stunned by the sudden death of his young wife, had gone for sympathy and distraction. Shortly before, it had been discovered that almonds, when triturated with alcohol, lost their bitter taste, which, however, was retained to a marked degree by amygdalin, the substance extracted by the alcohol. From this amygdalin, on treatment with boiling water, was obtained the long known bitter almond oil and prussic acid. The crude oil obtained from amygdalin, or directly from almonds, was distinguished by its power of absorbing oxygen from the air with formation of benzoic acid, and it was this fact which attracted Liebig and Wöhler's attention. They soon discovered that the production of benzoic acid was entirely independent of prussic acid, which, indeed, had no part at all in the composition of essential oil of bitter almonds. This oil, purified from all traces of prussic acid, benzoic acid, and water, formed the subject-matter of Liebig and Wohler's research. The first fact to be established was its composition, and for this they used the combustion method, which Liebig, after six years' constant thought and experiment, had finally perfected by the institution of potash bulbs for absorption of carbonic acid. The composition, read in terms of Berzelius' atomic theory, demanded a formula $C_{14}H_{12}O_3$, while the benzoic acid obtained by its immediate oxidation, its treatment with potash, or directly from gum benzoin, required the formula $C_{14}H_8O_4$, or $C_{14}H_{10}O_3$ if water of hydration was excluded. On passing chlorine through almond oil, hydrochloric acid was evolved and a body produced with a formula $C_{14}H_{10}O_2Cl_2$, which, in the presence of water, yielded benzoic acid and hydrochloric acid, and in the presence of alcohol, benzoic ether and hydrochloric acid. This chlorine derivative, the first acid chloride known, readily combined with ammonia to form a body analogous

Liebig and
Wöhler's
investiga-
tion of the
oil of
bitter
almonds.

¹ 3, p. 249.

to the oxamide discovered by Dumas in 1830, a body therefore which Liebig and Wohler termed benzamide, and which they found to have the composition $C_{14}H_{14}N_2O_2$. Benzamide boiled with potash solution yielded potassium benzoate and ammonia. Here, then, were a number of substances differing entirely from each other in their physical and chemical properties, yet agreeing in this, that fourteen atoms of carbon, ten of hydrogen, and two of oxygen, were represented in all their formulæ. Since all such substances were directly convertible into benzoic acid or its salts, these atoms probably entered their composition as a constant, self-sufficing group or radical. To this group the authors gave the name "benzoyl." "Your results are certainly the most important yet obtained in vegetable chemistry, . . . for which they mark the beginning of a new day," wrote Berzelius from Stockholm. "In Paris, the chemical world speaks only of your experiments. Come, then, with M. Wöhler, come and receive homage, your due," wrote Pelouze to Liebig. On the face of it there scarcely seemed sufficient reason for this excitement, yet a little thought will show how natural it was.

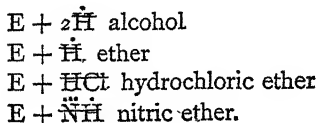
Recapitulation of previous views on organic constitution.

Forty years earlier, Lavoisier had introduced the idea of a "radical," a group of two or more atoms, which in organic nature took over the part played by single atoms in the mineral world. So sugar and oxalic acid he had regarded as different oxides of the same hydrocarbon radical. Berzelius had accepted Lavoisier's term, had spoken of that atomic group which was combined with oxygen in acids as a radical, but had gone no further, for he was convinced that such a radical could only combine in one proportion with oxygen, forming one substance, one acid. To the majority of chemists acceptance of such hypothetical units in organic substance seemed superfluous; the only so-called radical which was above suspicion was cyanogen—cyanogen the parent, not, however, of organic but of inorganic compounds. The conception of organic constitution which had seemed most fruitful was that which culminated in Dumas and Boullay's paper of 1828, that organic bodies were

compounded of other known, simpler, binary compounds. Ethylene did really combine with chlorine and hydrochloric acid, and was really obtainable from alcohol; its presence as such in Dutch liquid, ethyl chloride, alcohol, and so ether, did therefore seem probable. That chemical affinity depended on the electrochemical opposition of the atoms had been agreed by all who in anywise regarded chemical dynamics; so Dumas, to make his "hydrogène bicarboné" formula for sugar, $4C_2H_2\overset{\cdot}{C}\overset{\cdot}{H}H$, acceptable, must postulate unequal potentials in his different carbon atoms, while Berzelius, more consistent, must refuse any formula, unless oxygen alone be recognized as electrically antithetic to the rest of the compound. And finally, let it be remembered, isomerism was an established fact for all.

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Berzelius at first accepts the benzoyl radical, but speedily recants.



This was in the first burst of his enthusiasm, and it was not long before his electrochemical principles reasserted themselves. A radical is that which occurs combined with oxygen; a radical containing oxygen has no meaning; one might as well regard sulphurous acid as the radical of sulphuric, as

¹ Berzelius-Wöhler, *Briefwechsel*, i. p. 458.

to the oxamide discovered by Dumas in 1830, a body therefore which Liebig and Wohler termed benzamide, and which they found to have the composition $C_{14}H_{14}N_2O_2$. Benzamide boiled with potash solution yielded potassium benzoate and ammonia. Here, then, were a number of substances differing entirely from each other in their physical and chemical properties, yet agreeing in this, that fourteen atoms of carbon, ten of hydrogen, and two of oxygen, were represented in all their formulæ. Since all such substances were directly convertible into benzoic acid or its salts, these atoms probably entered their composition as a constant, self-sufficing group or radical. To this group the authors gave the name "benzoyl." "Your results are certainly the most important yet obtained in vegetable chemistry, . . . for which they mark the beginning of a new day," wrote Berzelius from Stockholm. "In Paris, the chemical world speaks only of your experiments. Come, then, with M. Wöhler, come and receive homage, your due," wrote Pelouze to Liebig. On the face of it there scarcely seemed sufficient reason for this excitement, yet a little thought will show how natural it was.

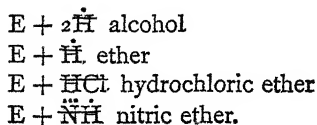
Recapitulation of previous views on organic constitution.

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¹ Berzelius-Wöhler, *Briefwechsel*, i. p. 458.

$C_{14}H_{12}O_2$ the radical of $C_{14}H_{12}O_3$. No; the radical of benzoic acid is $C_{14}H_5$, that of acetic acid C_4H_3 , and just as the former, benzoyl, is a common component of many bodies, so the latter, acetyl, is present in the vinyl chloride C_4H_3Cl of Regnault and the aldehyde $C_4H_3O.HO$ of Liebig. And now looking to ether and alcohol as represented by their simplest formulæ $C_4H_{10}O$ and C_2H_6O , Berzelius could not but regard the first as the lower oxide of the radical C_2H_5 , whose chloride is the well-known ether C_2H_5Cl , and the second as the oxide of a radical C_2H_6 . And to this view he henceforth steadfastly adhered.

Liebig inconsistent.

Meantime Liebig's attitude towards the constitution of acids had become a little mixed; for while he retained the benzoyl radical in its primitive entirety, he with Berzelius denied oxygen to the radicals of other acids, allowing acetyl to be the radical of acetic acid and the group C_2H to be the radical of both formic acid C_2HO and chloroform C_2HCl_3 . And in 1837 we find Dumas taking the same view of acid constitution, and writing those groups of atoms which enter into combination, some like oxygen or chlorine, some like a metal, as the true elements of organic chemistry.

Berzelius, Liebig, and Dumas have different opinions of the constitution of alcohol and ether.

Yet in giving a constitution to alcohol and ether Liebig and Dumas departed both from Berzelius and from each other. Berzelius, possessed by the antithesis of radical and oxygen, wrote ether $(C_2H_5)_2O$, and alcohol C_2H_6O ; Liebig, impelled by a desire for unity, and caring less for electrochemical theory than for the obvious relationship of the two substances, wrote ether $C_4H_{10}O$, and alcohol $C_4H_{10}O.H_2O$; Dumas, with a kindly feeling for his "hydrogène bicarboné" of 1828, continued to write $4C_2H_2.2HO$ and $2C_2H_2.H_2O$; and his discovery with Peligot of a body in wood spirit entirely analogous to alcohol and having the formula $C_2H_2.2HO$ seemed to many sufficient confirmation of his opinion. So while these chemists were at one in accepting radicals as the units of organic structure, they differed on the question of these radicals' composition, and, moreover, agreed to differ. The end to be achieved was not always the same; with one it might be a graphic presentment

of potential metabolism, with another a symbolic dissociation of matter into what were believed real, constant, simpler complexes. So, on the one hand, Dumas wrote alcohol $4C_2H_5, 2HO$, yet without suggesting that ethylene and water were present as such; on the other, Berzelius was prevented by the phenomena of isomerism from writing as a radical that which combined with oxygen merely because it did combine with oxygen—from writing either $C_4H_{10}O$ rather than $(C_2H_5)_2O$.

Liebig¹ suggested three conditions, two of which must be fulfilled by any group of atoms that would claim to be called a radical; it must occur unchanged in a number of compounds, it must be replaceable as such in these by single elements, and it must itself be capable of replacing elements. In fact, the very same arguments which were accepted as proving the existence of fluorine or calcium were to be regarded as equally cogent for the existence of radicals.

Liebig's
criterion of
a radical.

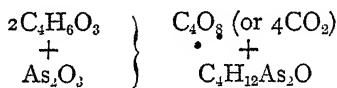
It was in 1843, on the consummation of Bunsen's research² into the cacodyl compounds, that the radical theory reached its zenith with the discovery of a three-element group capable of separate existence, and which in all its chemical relationships exactly impersonated a metal. Six years had Bunsen been engaged on his most difficult and dangerous task. Cadet's liquid, the body produced by heating arsenious acid with potassium acetate, had long had its place in chemical text-books, whose authors, held at bay by its spontaneous inflammability, its nauseous odour, and extraordinarily poisonous properties, had needs been content with describing it as a compound of acetic and arsenious acids. Analysis of Cadet's liquid by Liebig's method showed it to possess an empirical formula C_2H_5As ; its apparent analogy with alcohol C_2H_5O , and the mercaptan C_2H_5S discovered by Zeise in 1833, suggested to Bunsen the name "alcarsin," which combined the first letters of both alcohol and arsenic. Soon, however,

Bunsen's
research on
cacodyl.

¹ *Ann. Chem. Pharm.*, 25, p. 1.

² *Pogg. Ann.*, 40, p. 219; 42, p. 145. *Liebig's Ann.*, 37, p. 1; 42, p. 14; 46, p. 1.

considerations based on its vapour density rendered a doubling of the formula necessary, and this analogy vanished, though the name remained. Alcarsin was found to combine directly with oxygen, forming a substance "alcargen" with the formula $C_4H_{14}As_2O_5$, or perhaps $C_4H_{12}As_2O_4 + H_2O$, a body which possessed an acid reaction, and, curiously enough, was non-poisonous. Berzelius had indeed thought that alcarsin itself must contain oxygen, as the following equation would suggest:—



and now, on further examination, Bunsen found that this was the case. The purified alcarsin or cacodyl oxide, on the addition of hydrocyanic, hydriodic, and hydrochloric acids—the latter in presence of mercuric chloride—yielded a cyanide, an iodide, and a chloride respectively, all containing the group $C_4H_{12}As_2$; and, on heating the chloride to 100° with metallic zinc, clear prismatic crystals of the radical itself, $C_4H_{12}As$, or "Kd," were obtained. "The affinities of this radical, almost unexampled in the province of organic chemistry, the ease with which it can be transferred from one substance to another, the multiple relationships into which it enters with metalloids, but above all the electrochemical character of its compounds, mark an identity in the laws of organic and inorganic combination, which may not be without influence on our conceptions of a science whose propositions can scarcely be maintained unless with the weapons of analogy." So wrote Bunsen.

But much had happened during the years that Bunsen had devoted to his laborious task, much that had immediately to do with the combating of this very theory of radicals whose growth had been seemingly so sound and necessary. Let us go back, then, a decade, and, that our minds may acquire tone for the inception of quite different ideas, let us here dwell for a moment on the circumstances of a leading hero in the strife now raging.

What Liebig had done for Germany in the matter of instituting public laboratories, Dumas did for France. It is a strange fact that, up to 1832, when Dumas at his own expense opened a public laboratory, no provision had been made for the young, poor, and unknown scientific aspirant; this though for more than sixty years the world's eye had been turned, and rightly turned, Pariswards for the elucidation of physical problems. Nor could the want of political influence be urged in excuse for this neglect, for in no country at no time were high state offices so liberally distributed among men of scientific eminence. No, it was merely that to the outside world, and indeed to himself also, the man of science appeared as some one quite apart; he had always been self-made, outside the universities he must always be self-supporting. It was then right and good to divulge in brilliant lectures secrets wrested from nature; it was not right and good to foster enthusiasms which in many cases must necessarily lead to starvation.

Dumas
and the
institution
of public
labora-
tories in
France.

Jean Baptiste André Dumas was born on July 14, 1800, at Alais, in the department of Gard, where his father was town clerk. At fourteen years or thereabouts the boy was apprenticed to an apothecary, though not for long. Before his sixteenth birthday he had found his way to Geneva on foot, there to find inspiration in mere proximity to such men as De la Rive, Pictet, and de Candolle. Settled in the pharmaceutical laboratory of Le Royer, Dumas was rapidly acquiring local recognition as an independent worker, when Humboldt, on a visit to Geneva in 1822, called to see him. Some days spent in his company, listening to familiar talk of La Place, Berthollet, Gay Lussac, and other revered names, seemed to alter the complexion of things for Dumas. He must go to Paris. And to Paris he went, and—such was the impression he made—was soon installed in the chair of chemistry at the Athenæum. From this time on till his death in 1884 his life was one long and brilliant success. With the revolution of 1848 Dumas entered into the political life of his country, and during the years 1850–51 was Minister of

Dumas,
1800–
1884.

Agriculture and Commerce. He took his part, too, in municipal politics, and in 1859 was elected President of the Council of Paris. His hand may be traced in its present system of water supply, lighting, and drainage. A well-known writer¹ has spoken of Dumas as a man "blessed with a singularly equable temperament and a vigorous constitution, and with a nature as warm and sunny as that of his native province." Unfortunately such praises do not obliterate the effect of many and bitter animadversions² on his sense of priority rights and general equity as a man of science. Yet was Dumas a great man—a man to be judged by what he did, rather than by what he did not; a man to be honoured even among the honoured throng that made Paris the intellectual centre of the world.

Dumas
and sub-
stitution
in organic
com-
pounds.

Let us go back to the year 1834 and consider a group of facts, many of which, though well enough known, had hitherto appeared to call for no special attention, but which now awoke in Dumas³ an entirely new interest. It was in terms of the Berzelian theory of acids and of his own theory of the "hydrogène bicarboné" radical that he read these facts, and he made it a point that, but for this theoretical bias, his generalizations could never have been made.

1. Oxalic acid $C^4O^3.H^2O$, on the addition of nitric acid, was converted into carbonic acid C^4O^4 .

2. Anhydrous formic acid $C^4H^2O^3$ oxidized by mercuric oxide similarly yielded carbonic acid C^4O^4 .

3. By oxidizing alcohol $C^8H^8H^4O^2$, acetic acid $C^8H^8O^4$ or $C^8H^6O^3.H^2O$ was produced.

4. As shown by Faraday in 1821, Dutch liquid $C^8H^8Cl^4$, when exposed to the influence of chlorine in direct sunlight, was converted into a body with the formula $C^8Cl^8Cl^4$.

¹ Thorpe, *Essays in Historical Chemistry*, 1st ed., p. 298.

² Cf. E. Meyer, *A History of Chemistry*, p. 258.

³ *Ann. Chim. Phys.*, 2nd series, 56, p. 100; Dumas, *Traité de Chimie*, 5, pp. 99^b-102.

Similarly Gay Lussac obtained cyanogen chloride CyCl from hydrocyanic acid CyH ; and Liebig and Wöhler benzoyl chloride $\text{C}^{\text{B}}\text{H}^{\text{B}}\text{O}^{\text{B}}\text{Cl}^{\text{B}}$ from bitter-almond oil.

5. Finally Dumas had just discovered that by the action of chlorine on alcohol $\text{C}^{\text{A}}\text{H}^{\text{A}}\text{O}^{\text{A}}$ there was a body, chloral, produced with the formula $\text{C}^{\text{A}}\text{H}^{\text{A}}\text{O}^{\text{A}}\text{Cl}^{\text{A}}$.

It was on these facts and others similar that Dumas based what he called his "theory of substitution," a theory which comprised the three following rules:—

1. When a hydrogenized body is submitted to the dehydrogenizing action of chlorine, of bromine, of iodine, or of oxygen, it gains one atom of chlorine, bromine, iodine, or half an atom of oxygen for each atom of hydrogen it loses.

2. When the hydrogenized body contains oxygen, the same rule obtains without modification.

3. If the body contains water, the latter loses its hydrogen without replacement, and the body so obtained then obeys rule 2.

It is obvious, as Dumas subsequently contended, that here was no *theory* of substitution in the stricter sense, but rather a mere expression of ordered facts; these were facts of such significance, however, as to deserve classification under a special heading "metalepsy."¹

With us to-day the word "substitution" stands for so much that we are perhaps led to an undue appreciation of Dumas as the author of the "theory," which is the more unfortunate as we thereby detract from the merits of its virtual author, the far less known though scarcely less acute Auguste Laurent. As the latter long ago pointed out, and as the thoughtful reader will have discovered for himself, Dumas did no more than demonstrate the applicability of those laws of equivalence to organic composition, which Wenzel and Richter had discovered to obtain in the mineral world. Laurent² had been investigating the products of the action of chlorine on naphthalene, and in this same year, 1834, he told how these

Laurent
and sub-
stitution.

¹ *Mem. Acad.*, 15, 548.

² *Jour. de Pharmacie*, 1834. Laurent, *Chemical Method*, p. 186.

seemed to separate themselves into two classes, the one, that of the halydes, containing such compounds as $C_{10}H_8$, $C_{10}H_7Cl$, $C_{10}H_6Cl_2$, $C_{10}Cl_8$, and the other, that of the hyperhalydes, such compounds as $C_{10}H_8Cl_2$, $C_{10}H_8Cl_4$, $C_{10}H_7ClCl_3$, $C_{10}H_6Cl_2Cl_4$. The halydes might be distilled without decomposition, and were unchanged by potash; the hyperhalydes, on the other hand, when distilled, or treated with potash, lost hydrogen and chlorine as hydrochloric acid, a halyde remaining. So from the body $C_{10}H_8Cl_2$ he had obtained $C_{10}H_7Cl$; from $C_{10}H_8Cl_4$, $C_{10}H_6Cl_2$. It must be, thought Laurent, that the physical and chemical differences between the halydes and hyperhalydes are correlated with some difference in the structure of the molecules; it must be that the chlorine which enters into the composition of a halyde not only substitutes hydrogen, atom for atom, but naturally takes its place and to a certain degree fulfils its functions. So the chlor-compounds must be analogous with the compounds from which they are derived. These compounds, on the other hand, which the chlorine enters by addition rather than substitution, should be, and are entirely different. And just as Laurent had conceived turpentine and its allied halydes as an atomic group, $C_{10}A_8$, when A might be hydrogen or a halogen, so now he regarded ethylene as the mother of halydes, with the general formula C_2A_8 , which also would show a tendency to form hyperhalydes. Nor was it long before he and Regnault were successful in confirming all these conclusions.

Laurent's
theory of
nuclei.

In 1837 Laurent submitted a thesis to the "Faculté des Sciences" at Paris, which gave utterance to his more matured views on the phenomenon of substitution and its implications. The naphthalene group $C_{10}H_8$ is a nucleus, so is ethylene C_2H_4 . From these and similar "fundamental" nuclei are obtained "derived" nuclei by substitution; and from such "fundamental" and "derived" nuclei are obtained, by direct addition of hydrogen, halogen, or oxygen, a series of compounds which include such different bodies as hyperhydride, hyperhalyde, aldehyde and acid. So, taking ethylene as a "fundamental" nucleus, we have—

$C_4H_8.H_4$ ¹ the hyperhydride
 $C_4H_8.Cl_4$ the hyperhalide
 $C_4H_8.O_2$ the aldehyde
 $C_4H_8.O_4$ the acid

and to each of these series correspond others, where one, two, or more of the hydrogen atoms of the nucleus have been substituted by chlorine, without radical change in the properties of the derived compounds. It is by the careful consideration of this nucleus theory of Laurent that we more rightly understand the advance which had been made under the banner of substitution, and more nicely adjudicate the relative merits of its author and Dumas. True it is that this theory received but a cold reception; yet its place in the history of chemical philosophy is assured through Gmelin choosing it as the basis for classification of his great *Handbuch*, which, in the words of a contemporary,² "for completeness and fidelity of collation, for consecutiveness of arrangement, stands univalled."

The nucleus theory was unpopular; Berzelius remained contemptuously silent, while Liebig only noticed it with a view to chastening its author. But before long Berzelius was really stirred, for close on the publication of the nucleus theory came Malaguti's³ investigation of the simple and compound ethers. Ordinary ether $C_4H_{10}O$, under the attack of chlorine, yielded the chlor-ether C_4H_9OCl , and if combined with acetic acid, the body $C_4H_9O_2.C_2H_3O_2Cl$. The behaviour of both the free ethers and both the combined ethers respectively was entirely analogous. The chlorine atoms again played the part exactly of the hydrogen atoms they had displaced. Berzelius saw that here was the thin edge of a most potent wedge, which, unless immediately removed, might break down the whole fabric of that chemical theory he had spent so much on building. Misconceiving or ignoring Laurent's claims, he attributed its introduction to Dumas, to whom he read a lesson on the

Berzelius
 moved by
 Malaguti's
 investiga-
 tion of
 the simple
 and com-
 pound
 ethers.

¹ Laurent, *Chemical Method*, p. 195.

² *Quart. Jour. Chem. Soc.*, 7, p. 148.

³ *Ann. Chim. Phys.*, 64, p. 275.

first principles of chemistry, with the gist, black is *not* white, electro-positive is *not* electro-negative, nor can the electro-positive hydrogen take the place of and function as electro-negative chlorine. "I never said anything of the kind," answered Dumas.¹ "To represent me as saying so is to attribute to me an opinion against which I protest most strongly. . . I am not responsible for the gross exaggerations with which Laurent has invested my theory."

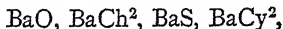
Dumas' work on chloracetic acid.

Then Dumas himself saw and believed. He was engaged by the action of chlorine on acetic acid,² when, with much evolution of hydrochloric and carbonic acids, there was produced a deliquescent solid, whose vapour density demanded the formula $C_2H_3ClO_2 \cdot H_2O$, which retained the acidic properties of acetic acid, forming a silver salt $C_2H_3ClO_2 \cdot AgO$, a methylic ether $C_2H_3ClO_2 \cdot C_4H_9O$, and which, on decomposition with ammonia, produced chloroform, $C_2H_3Cl_3$, and ammonium carbonate, just as the mother acid produced the hydrocarbon C_2H_6 . Here was a compound produced by substitution of chlorine atoms for hydrogen, which retained the acid character, the saturation capacity, and potentialities for decomposition of its mother substance. It must be, Dumas now allowed, with a tribute to Laurent's prevision, that position rather than character of atoms governs the properties of a chemical substance.

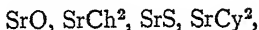
The organic molecule conceived spacially.

Laurent, in 1837, striving after the real truth of substitution, had pictured the organic molecule as a prism, the angles of which were occupied by carbon atoms, the centres of its edges by hydrogen atoms, or, failing these, by chlorine, bromine, or iodine atoms. Dumas now, in 1840, discovers a parallel to his conception of organic composition in the theory of the planetary system, a system where stability depends not on the intrinsic nature of the planetary units, but on their relative position to themselves and to the sun. Laurent's prismatic molecules had become "nuclei" of a series of compounds associated by their common origin; Dumas' planetary molecule is discovered to be the "type" of a number of compounds likewise associated.

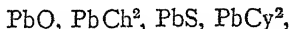
In inorganic chemistry we have different compounds of the same metal belonging to the same type; thus—



with which we may compare—



or—



and so, too, in organic. "One¹ may take the group C_4H_2 as the point of departure, and combine it successively with H_6 , Ch_6 , and O_3 ; or, rather, one may take H_6 and unite it with C_4H_2 , C_{24}H_6 , etc., and there will result groups of bodies allied by a great number of common properties, and appertaining all to one large chemical type, susceptible of subdivision into particular series, founded on one or other of the indicated bases." Hence we arrive at a "veritable natural classification." Substances like marsh gas C_4H_8 and chloroform $\text{C}_4\text{H}_2\text{Cl}_6$, acetic acid $\text{C}_8\text{H}_8\text{O}_3 \cdot \text{H}_2\text{O}$ and chloracetic $\text{C}_8\text{Cl}_6\text{O}_3 \cdot \text{H}_2\text{O}$, aldehyde $\text{C}_8\text{H}_{10}\text{O}_2$ and chloraldehyde $\text{C}_8\text{H}_2\text{Cl}_8\text{O}_2$, are respectively of the same "chemical type." Substances like alcohol, $\text{C}_8\text{H}_8 \cdot \text{H}_4\text{O}_2$, and acetic acid, $\text{C}_8\text{H}_6\text{O}_3 \cdot \text{H}_2\text{O}$, producible from one another by substitution, and containing the same number of equivalents, yet exhibiting essentially different properties, are of the same "mechanical type."

Here is an extract² from Dumas' table :—

FIRST MECHANICAL TYPE

				Alcohol type		Acetic type
Formic series	$\text{C}_4\text{H}_6\text{O}_2$...	$\text{C}_4\text{H}_2\text{O}_4$
Benzoic series	$\text{C}_{28}\text{H}_{16}\text{O}_2$...	$\text{C}_{28}\text{H}_{12}\text{O}_4$

SECOND MECHANICAL TYPE

				Ether type		Aldehyde type		Acid type
Formic series	$\text{C}_4\text{H}_6\text{O}$...	$\text{C}_4\text{H}_4\text{O}_2$...	$\text{C}_4\text{H}_2\text{O}_3$
Benzoic series	$\text{C}_{28}\text{H}_{14}\text{O}$...	$\text{C}_{28}\text{H}_{12}\text{O}_2$...	$\text{C}_{28}\text{H}_{10}\text{O}_3$

¹ Dumas, *Mémoires*, p. 28.

² *Ibid.*, p. 86.

THIRD MECHANICAL TYPE

Formic series ^{defiant type} C_4H_4
Benzoic series $C_{24}H_{12}$

The advance marked by the type theory.

One observes that Dumas' mechanical types associate the same compounds as Laurent's series; the difference being that while Laurent's compounds were produced by addition to a nucleus, Dumas' resulted from substitution in the typical substance. Where, then, lay the advance¹ claimed with this type theory of Dumas? First, in this, that substitution by equivalents, and in the sense of Laurent, was more rigorously insisted on; secondly, in that the necessity of showing bodies of the same "mechanical type" to be composed of the same number of equivalents rendered the question of their real molecular weights more acute; thirdly, in that its conception brought Dumas to throw down the gauntlet to Berzelius in the arena of the electro-chemical school; and lastly, in the pre-eminent scientific position of its author, which gave its status at least respectability, indeed attracted to it wide and conscientious consideration. Yet to the outside world the demands of the French school seemed undue; even the patient Wöhler was tired of the eternal song of substitution, though, as he wrote² to Berzelius in 1840, he had himself been led to try his hand at the new process. He had heated copper acetate $CuO + C_4H_6O_8$ in a stream of chlorine, again treated the body so produced with the same element, and finally obtained pleasing yellowish crystals of a compound $ClCl + Cl^4Cl^3 + H$. Amidst a pæan of triumph from Berzelius, Liébig, and their followers, an account of a very similar success found its way into the chemical journals.

Berzelius attacks the problem of substitution.

But it was not in Berzelius' nature to be merely a destructive critic; he recognized the moment of Dumas' results, and saw that the body of French opinion was likely to

¹ Cf. Kekulé, *Lehrbuch*, i. p. 79.

² Berzelius-Wöhler, *Briefwechsel*, ii. p. 163.

exert a powerful if merely temporary influence on scientific thought. He had approached the question in a candid spirit, had examined acetic and chloracetic acids to satisfy himself if in very deed their properties showed analogy; had discovered they did not, and must now provide his kingdom, the chemical world, with formulæ reconciling all the facts, old and new. Let us again consider Berzelius' point of view: all substances, organic and inorganic, result from the combination of two units, the one electro-positive, the other electro-negative; these units, once positive or once negative, are always positive or negative, and the parts played by them are always antithetic.

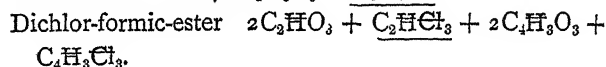
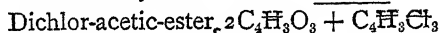
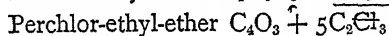
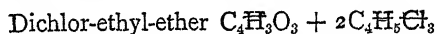
Acetic acid has the formula $\overset{+}{\text{C}}_2\overset{+}{\text{H}}_3\overset{-}{\text{O}}_3$, its hydrate the formula $\overset{+}{\text{C}}_2\overset{+}{\text{H}}_3\overset{-}{\text{O}}_3\overset{+}{\text{H}}\overset{-}{\text{O}}$. If this or other compound is exposed to the action of chlorine and chemical change occurs, it can only be by the exchange of negative oxygen for negative chlorine, or by a general disruption of the compound, combination of chlorine as negative unit with another and positive, as hydrogen, carbon or hydrocarbon, and consequent production of a molecule self-sufficing, or one which combines further with a second molecule, resulting from the dualistic combination of residual atoms. So from acetic acid $\overset{+}{\text{C}}_2\overset{+}{\text{H}}_3\overset{-}{\text{O}}_3\overset{+}{\text{H}}\overset{-}{\text{O}}$ we obtain not $\overset{+}{\text{C}}_2\overset{+}{\text{Cl}}_3\overset{-}{\text{O}}_3\overset{+}{\text{H}}\overset{-}{\text{O}}$, but $\overset{+}{\text{C}}_2\overset{+}{\text{Cl}}_3 + \overset{-}{\text{C}}_2\overset{-}{\text{O}}_3\overset{+}{\text{H}}\overset{-}{\text{O}}$, a compound then of oxalic acid and perchloride of carbon with water of hydration. But in 1842 Melsens¹ conclusively demonstrated a relationship between acetic acid and its chlorinated derivative, by showing that an aqueous solution of the latter was converted into the former by the action of potassium amalgam. Berzelius was nothing daunted. For long had the basic properties of the alkaloids been ascribed, and seemingly with reason, to the presence of ammonia as such in their composition; only eight years before had Mitscherlich shown how sulphuric acid retained its saturation capacity to the full even after combination with benzoic acid—a fact only to receive graphic explanation by adopting the formula $\overset{+}{\text{H}}\overset{+}{\text{S}} + \overset{-}{\text{Bz}}\overset{-}{\text{S}}^2$ for the body so obtained; and Liebig's mandelic acid $\overset{+}{\text{C}}_{14}\overset{+}{\text{H}}_8\overset{-}{\text{O}}_2 + \overset{-}{\text{C}}_2\overset{-}{\text{H}}\overset{-}{\text{O}}_3\overset{+}{\text{H}}\overset{-}{\text{O}}$,

¹ *Ann. Chim. Phys.* (3), 10, 235.

² Berzelius, *Lehrbuch*, i. p. 182.

a compound, therefore, of bitter almond oil and formic acid, was yet another case in point. There are, then, said Berzelius, substances produced by "copulation," to use Gerhardt's² term; there are "copulated" compounds containing an active component and a passive, the latter exerting but an insignificant influence on the properties of the whole. In the cases cited, the organic radical, the benzoic acid, and the almond oil are the "copulæ," the ammonia, the sulphuric, and the formic acids the active components. So acetic acid was oxalic copulated with a hydrocarbon, and it mattered little whether the hydrocarbon copula was converted into a carbon chloride or not, as long as the properties of the active component, oxalic acid, remained constant. Acetic acid being represented by the formula $C_2H_3O_3.HO$, chloracetic must be $C_2Cl_3.C_2O_3.HO$.

Here are more of Berzelius' formulæ:—



"To make acetanilide,¹ he no longer employed acetic acid and aniline, but he recopulated a copulated oxalic acid with a copulated ammonia." And yet, while Berzelius was staking his all on the truth of his electro-chemical theory, doubling, trebling, and quadrupling formulæ with none of his former sense of the cogency of simplicity, and directing operations from the desk rather than from the laboratory, he was, nevertheless, accepting the very truth which made his principle untrue—he was accepting substitution *in the copula*. Berzelius was left to fight his battle alone, and it was a forlorn hope. Even Liebig had deserted him. Chlorine could take the place and play the part of manganese, why should it not do the same for hydrogen also? And he had gone over to the side of Dumas.

¹ Blomstrand, *Chemie der Jetztzeit*, p. 79.

² Laurent, *Chemical Method*, p. 204.

CHAPTER IX

THE CONSTITUTION OF ACIDS AND THE DIFFERENTIATION OF THE TERMS ATOM, MOLECULE, AND EQUIVALENT . .

ATTACHMENT to Lavoisier's dogma, experience, and his electro-chemical theory prevented Berzelius' accepting for long any substance as an acid which was not an oxide. This oxide, this acid, might combine with water; it might combine with base, and here sometimes in two proportions, producing bodies formulated $\text{H}\cdot\ddot{\text{S}}, \ddot{\text{M}}\ddot{\text{S}}^2, \ddot{\text{M}}\text{S}^4$ in the case of sulphuric acid, $\text{H}\cdot\ddot{\text{C}}, \ddot{\text{M}}\ddot{\text{C}}^2, \ddot{\text{M}}\text{C}^4$ in the case of carbonic. Those were the neutral salts in which were combined one equivalent of base, $\ddot{\text{M}}$, and one equivalent of acid, $\ddot{\text{S}}$ or $\ddot{\text{C}}$. If there were two equivalents of acid, the salt was acid; if two of base, the salt was basic. Finally, the maintenance of some simple ratio between the number of oxygen atoms in base and in acid was the most important criterion of the correctness of formula for any particular member in any particular series, neutral, acid, or basic. But in 1816 Berzelius found that the formulæ for the neutral phosphates must be of the type $\ddot{\text{M}}\ddot{\text{P}}$, that the ratio between the number of oxygen atoms of base and acid was here not simple. The phosphates, and the arsenates too, were then exceptions to his oxygen law and to his law of neutrality. Again, in 1826, when Berzelius introduced the conception of sesquioxides, he was compelled to such formulæ as $\ddot{\text{M}}^2\ddot{\text{S}}^3$; to an admission of neutrality not necessarily depending on acid and base being present in equivalent proportions. Yet most salts did obey both the oxygen law and law of equivalents.

Berzelius' opinion of acids and salts.

The
hydracid
theory of
Davy and
Dulong.

Just as Berzelius was led to an unreserved generalization from his theory of electro-chemical reaction, so Davy, moved by his recognition of the elementary nature of chlorine, came in 1810 to consider acids and salts, haloid or amphoteric, as constituted similarly, depending respectively on their hydrogen or metallic constituent for acidic or saline character. He had found that the oxide of iodine was by no means acidic till it had combined with water, that the reactive character of muriatic acid and its salts was in nowise altered by the addition of oxygen. In his opinion division of this oxygen between metal and chlorine, as Berzelius' theory demanded, seemed uncalled for. Davy did not, however, regard acids and salts as composed binarily of hydrogen or metal on the one hand, and electro-negative radical on the other; rather that chlorine, oxidized iodine, the compound of sulphur and oxygen, were of such a nature that, combined with hydrogen ternarily, they produced an acid. Dulong's examination of oxalic acid in 1815 had brought him to regard this substance as composed of carbonic acid and hydrogen, and, being acquainted with Davy's views, to see then in hydrogen alone the acidifying element. Yet, inherently reasonable as seemed this hydracid theory of Davy and Dulong, and respected as it was, for both sponsors had great names, it did not become popular. To the electro-chemical school, for years the only school, an electro-chemical antithesis between water and acid, base and acid, was so obvious, and so many anhydrous acids were objects of everyday examination, that no end at all, unless one purely schematic, was served by postulating such radicals as were combined with hydrogen on the Davy-Dulong system.

Berzelius
open-
minded.

In 1833, when the reasoning power of his logical mind was at its very zenith, Berzelius was not going to maintain that acid and oxide did as such exist in salts; that the great end might not be equally served by regarding selenate of tin as $\text{Sn} + \text{SeO}_4$, $\text{SnO} + \text{SeO}_3$, $\text{SnO}_2 + \text{SeO}_2$, or $\text{SnSe} + 4\text{O}$, provided one remained constant to a single type. He made the reservation, however, that such cases as the isomerism of the selenite of stannic oxide and selenate of stannous oxide must find voice

in correlated formulæ. Yet so many salts were producible by the combination of a known oxide with a known so-called acid, that to lesser minds such doubts seemed superfluous. A neutral salt is one composed of an equivalent of acid and an equivalent of base; do let us be consistent and write, therefore, aluminium oxide $\text{Al} + \text{O}$ and phosphoric acid $\text{P} + 2\frac{1}{2}\text{O}$! Such was the attitude of Gay Lussac and Gmelin.

Thomas Graham¹ was born in Glasgow in 1805. His father was a manufacturer of sufficient means to give the boy a good education, and at the age of fourteen young Graham was sent to his native university; he graduated five years later. In Glasgow there was a public laboratory, the first to have been instituted for the purpose of general instruction in Great Britain; and it was at the feet of its founder, Dr. Thomas Thomson, that Graham learnt the elements of chemistry. Thomson was a confirmed atomist and a great teacher, and his influence is easily traceable in the issues of his pupil's life-work. Graham's father had decided that his son should enter the ministry; but the boy knew himself better; he would employ his life in solving some of those problems old Thomson had suggested. His mother stood by him, and he went to Edinburgh to learn more of the science he had at heart.

Graham,
1805-
1869.

In 1829 Graham was appointed lecturer in chemistry to the Glasgow Mechanics' Institute, and the year following he accepted the similar post at Anderson's College. He had now a laboratory at his disposal, poorly furnished perhaps, but sufficient to allow his watching gases diffuse and phosphoric acid dehydrate. And seven years later he was in London, Professor of Chemistry at its newly founded university. He had not been in London long—only four years—when he was made president, first president, of a new society in the creation of which he had been very strenuous, the Chemical Society of London. Such work as Graham's demanded recognition, and in 1854 he was made Master of the Mint. And now for six

years his voice was silent: Graham was conscientious, and he was Master of the Mint; conscience multiplied the duties of office, the tenor of his past life and character of his mind made them onerous. But from 1860 onwards—he died in 1869—he again found leisure, leisure to devote himself to his beloved science; and with lively mind preying on feeble body, he lived out a life to be honoured always and by all who would honour chemical science.

Graham's
work on
the phos-
phates and
arsenates.

A very real interest in the structure of the oxyacids was quickened in 1833 by Graham's paper¹ on the phosphates and arsenates. The modification in properties which common phosphate of soda undergoes on strongly heating had been described by Clark in 1828, and it was this modification which spurred Graham to his task. His facts were these: the bi- or superphosphate of soda is associated with four atoms of water, two only of which are lost at the temperature 212° , a third not till the temperature is raised to 400° , when a substance remains differing from the original phosphate in giving a white and granular precipitate with silver nitrate, containing two atoms of silver oxide to one double atom of phosphoric acid. On heating the pyrophosphate of soda so obtained to redness the last atom of water is lost, and a salt is obtained, readily yielding a solution with water which gives a gelatinous precipitate with silver nitrate and coagulates albumen; and this metaphosphate, heated to 400° , reproduces the pyrophosphate from which it was obtained, but only when water is also present. Whatever be the modification of phosphoric acid we choose, if it is fused with soda or its carbonate, we shall obtain a meta-, pyro-, or ordinary phosphate according as we employ one, two, or three proportions of the alkali. Conversely, however much heated, the sub-phosphate of soda will not yield a pyrophosphate, nor the common phosphate a metaphosphate.

Graham could meet these facts with only one theory—the theory that water acting simultaneously and concurrently with soda was present as a constitutional asset in the atom of the

¹ *Phil. Trans.*, 1833, p. 253.

phosphate and pyrophosphate. He therefore wrote the following formulæ:—

Superphosphate of soda, $\text{Na}\dot{\text{H}}^2\ddot{\text{P}} + \dot{\text{H}}^2$; the yellow precipitate of silver phosphate, $\text{Ag}^3\ddot{\text{P}}$; phosphoric acid, $\dot{\text{H}}^2\ddot{\text{P}}$.

Pyrophosphate of soda, $\text{Na}\dot{\text{H}}\ddot{\text{P}}$; the white and granular silver pyrophosphate, $\text{Ag}^2\ddot{\text{P}}$; pyrophosphoric acid, $\dot{\text{H}}^2\ddot{\text{P}}$.

Metaphosphate of soda, $\text{Na}\ddot{\text{P}}$; gelatinous silver metaphosphate, $\text{Ag}\ddot{\text{P}}$; metaphosphoric acid, $\dot{\text{H}}\ddot{\text{P}}$.

Here, then, was ratification of the dualistic conception, seeming destruction to a belief in the anhydrous acid, and great discomfiture to the few upholders of the hydracid school; for, as Dumas pointed out in 1836, it was surely unreasonable, in view of the ready convertibility of one acid into the other, to postulate the existence of three new radicals PO_3 , PO_7 , PO_6 , to suit the formulæ H_3PO_3 , H_2PO_7 , and HPO_6 .

During the next year, 1838, Dumas met Liebig, and was converted to a belief in the radical theory. The two decided to join forces and solve the problem of organic constitution by discovering the proximate constituents or radicals of organic compounds. Graham's work had made a lasting impression on Liebig's mind, and suggested problems which were a great incentive to this conjunction. But Liebig and Dumas were not a pair to run easily in double harness. The one paper, however, which appeared immediately under their joint names, was important enough, for it went to show that citric acid in its behaviour towards a base was very similar to hydrated phosphoric acid. In fact, the effect of heat on its crystalline salts was not at all consistent with Berzelius' formula $3(\text{C}_4\text{H}_4\text{O}_{11} + \text{MeO})$, for they lost water at a temperature of 190° without undergoing modification in any particular which would suggest constitutional change; such citrates must then be written $(\text{C}_{12}\text{H}_{10}\text{O}_{13}\text{MeO}) + \text{H}_2\text{O}$. A neutral salt by the union of three atoms of base with one of acid! "Unthinkable," said Berzelius.¹

Liebig and Dumas examine the citrates.

¹ Berzelius-Liebig, *Briefwechsel*, p. 158.

This dehydrated body must be $2(\text{C}_4\text{H}_4\text{O}_4 + \text{MeO}) + (\text{C}_4\text{H}_2\text{O}_3 + \text{MeO})$. But Liebig was not to be denied, and in 1838 appeared his classic work, "On the Constitution of Organic Acids." ¹

Liebig on
the con-
stitution
of organic
acids.

Liebig had found that the meconic acid of opium gave precipitates with silver nitrate whose composition, varying with the conditions of the experiment, might respectively be expressed $\text{C}_{14}\text{H}_2\text{O}_{11} \cdot 3\text{AgO}$, and $\text{C}_{14}\text{H}_4\text{O}_{12} \cdot 2\text{AgO}$. Comparison with the formula of the acid itself $\text{C}_{14}\text{H}_8\text{O}_{14}$ discovered that combination with one or several atoms of base implied elimination of one or several atoms of water. After persistent boiling with concentrated hydrochloric acid, meconic acid yielded another substance, comenic acid, which also combined with silver oxide to form two salts, $\text{C}_{12}\text{H}_4\text{O}_8 \cdot 2\text{AgO}$ and $\text{C}_{12}\text{H}_6\text{O}_9 \cdot \text{AgO}$; and both meconic and comenic acids on distillation produced a pyrocomenic acid, capable of combining with one proportion of silver oxide only, to form a body $\text{C}_{10}\text{H}_6\text{O}_5 \cdot \text{AgO}$. Analogous results he obtained with cyanuric and citric acid. Let us compare, then, said Liebig, the formulæ which Graham has suggested for the three phosphoric acids, which, after all, are merely expressions of experimental fact, with those suggested by these later experiments. We have—

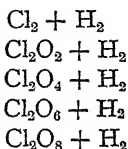
Phosphoric acid	$\text{P}_2\text{O}_5 + 3\text{Aq.}$
Pyrophosphoric acid	$\text{P}_2\text{O}_5 + 2\text{Aq.}$
Metaphosphoric acid	$\text{P}_2\text{O}_5 + \text{Aq.}$

Cyanuric acid	$\text{Cy}_6\text{O}_3 + 3\text{Aq.}$
Fulminic acid	$\text{Cy}_6\text{O}_3 + 2\text{Aq.}$
Cyanic acid	$\text{Cy}_6\text{O}_3 + \text{Aq.}$

Meconic acid	$\text{C}_{14}\text{H}_2\text{O}_4 + 3\text{Aq.}$
Comenic acid	$\text{C}_{12}\text{H}_4\text{O}_8 + 2\text{Aq.}$
Pyrocomenic acid	$\text{C}_{10}\text{H}_6\text{O}_5 + \text{Aq.}$

Citric acid	$\text{C}_{12}\text{H}_{10}\text{O}_{11} + 3\text{Aq.}$
First pyrocitric acid	$\text{C}_{10}\text{H}_8\text{O}_6 + 2\text{Aq.}$
Second pyrocitric acid	$\text{C}_8\text{H}_4\text{O}_6 + \text{Aq.}$

There can be no question of dividing the electro-negative component by three or two, and so offering an atom of acid which does combine with one atom of water or base, for even where this is possible atomically, the existence of such salts as $\text{Cy}_6\text{O}_3 \left\{ \begin{smallmatrix} 2\text{AgO} \\ \text{KO} \end{smallmatrix} \right.$ makes it unreasonable. Yet one cannot suggest that the mere abstraction of one or two atoms of water from phosphoric acid can so modify its properties as we see them modified in pyro- or meta-phosphoric acid. Phosphoric acid, indeed, is a crucial instance, and whatever theory we adopt to explain its curious metamorphoses we must apply to all other acids equally, be they tri-, di-, or mono-basic—such were the adjectives by which Liebig differentiated the acids which formed salts with separation of three, two, and one atom of water respectively. What are the facts? An acid, on heating, loses water, and simultaneously saturation capacity; why? The acid so formed does not take up water on solution and so regain its saturation capacity; why? The anhydrous acids do not combine with bases, yet they do so after these have combined with water; why? Silver oxide is less electro-positive than potassium or sodium oxides, yet it always replaces three atoms of water in phosphoric acid which the others do not; why? It may appear a consigning of the whole science to topsy-turvydom, but one must allow that the hydracid theory of Davy alone meets the facts. The hydracid theory has, indeed, already been admitted for sulphocyanic acid, and its formula written $\text{Cy}_2\text{S}_2\text{H}_2$ —how otherwise could one have understood the separation of lead from a body CyS.PbS by sulphuretted hydrogen?—yet has been denied in writing the analogous cyanic acid $\text{CyO.H}_2\text{O}$. And consider the series of acids—



all of which exhibit identical saturation capacity. It matters not whether a base is offered to any oxy- or haloid-acid; in either case water is separated. Who is to say that in one case the water is merely separated, in the other is first formed by combination? Indeed, it cannot longer be doubted that saturation capacity depends on hydrogen alone, that it has no relation whatever to the character of the acid radical. Let us, then, write the phosphoric acids $P_2O_8 + H_6$, $P_2O_7 + H_4$, and $P_2O_6 + H_2$ respectively; the acids of the cyanuric group, $Cy_6O_6 + H_6$, $Cy_4O_4 + H_4$, and $Cy_2O_2 + H_2$; of the meconic, $C_{14}H_2O_{14} + H_6$, $C_{12}H_4O_{10} + H_4$, $C_{10}H_6O_6 + H_2$; of the citric, $C_{12}H_{10}O_{14} + H_6$, $C_{10}H_8O_8 + H_4$, and $C_5H_4O_7 + H_2$ respectively. Here is a conception which, in any case, brings us nearer the unification of our science. Is it just? Who can say? "It is through darkness that one journeys to the light."

A knowledge of polybasicity, and the differentiation of atom, molecule, and equivalent first attained through the study of organic chemistry.

If it was work more especially in the domain of organic chemistry which first defined and ratified the previous vague impression of that something we now call polybasicity, it was no less in the province of organic compounds that a paramount need for the differentiation of those all so important terms atom, molecule, and equivalent was first discovered. That this should have been so in the first case we are not surprised, remembering how entirely the whole science of inorganic chemistry was involved in a certainty of the dualistic constitution of salts, a certainty impressed by Berzelius, a master of his subject, catering for all the philosophic needs of his less endowed scientific brethren. Nor should we be surprised in the second case. It had mattered little, where no reference was made to the unit as impelling and governing combination, whether this unit was taken as present in a particular compound singly, or in groups of two, three, or four. If one was considering organic compounds, one might take 12 or 6 or 3 as the combining unit of carbon indifferently; all one wanted was some unit in terms of which to formulate, and all attempts at classification previously made, though quite local, had been to themselves consistent and so far satisfactory.

What was becoming, however, a very real need through the daily additions to the already swollen list of organic compounds was some general principle by which to select the right multiple of the empirical formula, that each inquirer, using what atomic or equivalent values he would, might classify more generally and with reasonable security. It was only the feeling of the vastness of his subject and the necessity for the co-operation of all working in absolute unison, that made Laurent¹ say in 1853, "It is necessary that the proportional numbers of the simple bodies should be fixed for a period at least of ten, twenty, or thirty years, and that all chemists should employ these numbers." Yet an international meeting called to Karlsruhe seven years later, with the special object of so fixing these numbers, could agree on but one point, that each investigator must have complete freedom in this matter of formulation. However, nine years before Laurent made his modest demand, Gerhardt had supplied the general principle needed for a consistent though personal formulation, and recognition of this principle had brought Laurent to our present-day conceptions of atom, molecule, and equivalent. The recognition and exercise of this principle—the referring of all formulæ to the relative weights of two volumes of their vaporized correlate—makes Gerhardt responsible for one of the great stages by which organic chemistry had advanced.

When Gerhardt began his work, there were three systems of chemical equivalents; the first, that favoured in Germany and England, whose chief exponent was Gmelin; the second, that of Berzelius; the third, whose home was France, and whose chief patrons were Dumas and Laurent. The relationship between the three will appear on examination of the values—

Chemical equivalents prior to Gerhardt.

¹ *Chemical Method*, p. 7.

H	N	Cl	C	O		Water	Carbonic acid	Methane
I 5 (H=1)	I4 7 (N=14)	35.5 17.75 (Cl=35.5)	6 6	8 8	Gmelin Berzelius { Dumas and Laurent }	HO HO	CO ₂ CO ₂	C ₂ H ₄ C ₂ H ₂
I"	I4	35.5	3	8		HO	C ₂ O ₂	C ₂ H ₂

The difference between the numbers of Berzelius and Gmelin is more apparent than real; and indeed the latter would have regarded them as identical, allowing the bar which Berzelius had introduced to suggest combination by double atoms, by equivalents, to have no meaning. The values given by Dumas and Laurent allowed of a real equivalent notation; the value 3 for Carbon resulted from acquiescence in Gay Lussac's belief that equal volumes of carbon vapour and oxygen combined to form carbonic acid. It must be carefully borne in mind that, though Berzelius, and many chemists with him, regarded those weights of the gaseous elements which occupy equal volumes as the atomic or equivalent weights, the same by no means followed for the atomic weights of their several compounds; it was only necessary here that there should be a simple ratio between the volumes occupied. As a matter of fact, however, the atomic formulæ of inorganic compounds—water, carbonic acid, the oxides of sulphur, for example—did represent the weights present in equal volumes of their vapours; they might all be taken as representing two volumes. But this was by no means so for organic bodies.

Gerhardt and the formulæ of carbonic acid and water.

In 1841 very little doubt existed that, certainly in the case of many organic acids, an accurate atomic formula had been arrived at. Such, in the case of acetic and salicylic acids, were those which represented the hydrated acids as containing one atom of water, C₄H₃O₃.HO and C₁₄H₅O₅.HO respectively, which symbolized the weights present in four volumes of their vapours, the formulæ CO₂ and HO representing two volumes. But Gerhardt discovered that when these two substances,

acetic and salicylic acid, were heated with soda lime, with the production of methyl hydride and carbolic acid respectively, there was also produced, from four volumes of the acids, carbonic acid, which would occupy four volumes; that, indeed, whenever carbonic acid was produced by decomposition of an organic compound, it was always in quantities represented by four volumes or some multiple of four volumes. When water, too, was eliminated, Gerhardt always found quantities corresponding to four volumes, or some multiple of four volumes, as was also the case with hydrochloric acid and ammonia. Using Dumas' and Laurent's equivalents then, the atoms of carbonic acid, water, hydrochloric acid, and ammonia were to be symbolized thus, C_4O_4 , H_4O_2 , H_2Cl_2 , N_2H_6 ; for it were absurd to suppose that if quantities represented by C_2O_2 , H_2O , HCl , and NH_3 existed, they would never have been evolved in the multifarious operations he had conducted. Yet these latter formulæ were those which in very deed did express those quantities evolved on the decomposition of a compound inorganic atom. The fact was, as Gerhardt pointed out, chemists had been using two different schemes of equivalents for the atoms of organic and inorganic compounds; the formulæ of the first had been based on the hypothesis that $O = 16$, of the second that $O = 8$, and so identical formulæ had been ascribed to the carbonic acid and water from both organic and inorganic compounds. But that the oxygen of organic and of inorganic compounds should possess different atomic values outraged common sense. The only possible thing to do was to accept a four-volume standard for the atoms of inorganic compounds also, and write carbonic acid and water C_4O_4 and H_4O_2 , or a two-volume standard for the organic atoms, and write C_2O_2 and H_2O . It was the pernicious theory of dualism that was at the bottom of the difficulty, the necessity of accepting formulæ for acetic and salicylic acids, for example, which implied the presence in them of an atom of water. Yet if an atom of water, representing four volumes of its vapour, was to be formulated H_4O_2 , how could an atom of acetic acid, similarly representing four volumes, be formulated $C_4H_6O_2.H_2O$,

as analysis demanded? Gerhardt chose the two-volume standard, writing therefore water H_2O . He had cogent simplicity on his side; moreover, the sums of the densities of the elements present in compounds were severally the double of the molecular weights based on his assumption.

Gerhardt's
new equi-
valents.

The ratio 1 : 16 between the equivalent, atom, or volume weight of hydrogen and oxygen,—Gerhardt regarded all these terms as synonymous,—which the formula H_2O demanded, was identical with that proclaimed by Berzelius, 0.5 : 0.8, yet Gerhardt would allow nothing in common between the two systems. He never made it quite clear why he doubled the atomic weights of hydrogen and oxygen rather than halve the atomic formulæ of their respective compounds, preserving the old values; but it is likely he thought he was thereby dealing a blow at the barred formulæ of Berzelius. Berzelius had written H as the real equivalent of hydrogen, but retained H as the expression of its atomic weight. Gerhardt took the value of H for the equivalent or atomic weight of hydrogen, writing it H , and discrediting belief in potential subdivision. The equivalent weight 16 for oxygen was alone consistent with the presence of two atoms of that element in carbonic acid; but, on the other hand, there was no reason against multiplying the equivalent of carbon by two, and so making it equal 12, which would necessitate the formula CO_2 for carbonic acid. The value 16 being given to the atom of oxygen, Gerhardt had now to make sulphur 32 and selenium 82, while the equivalents 35.5, 80, and 14 for chlorine, bromine, and nitrogen followed from the volumetric composition of their hydrogen compounds. The compounds which hydrogen and the metals formed with other elements Gerhardt regarded as completely analogous, those with oxygen must have the general formula R^2O , acids and salts formulæ differing only through the substitution of one, two, or three atoms or equivalents of hydrogen, according as the acid was mono-, di-, or tri-basic, for one, two, or three atoms or equivalents of metal. The weights of the silver, potassium, sodium, and other metallic atoms were consequently halved. One would think that this new system of Gerhardt

would have found a warm welcome in France, the home of equivalent weights; but it was not so. Gerhardt himself was inconsistent in allowing such formulæ as H_2O , Ag_2O in an equivalent system; these should certainly have been written HO and AgO , as his seniors had long written them; and Gerhardt was too young to be allowed any latitude in consistency.

There was probably but one man in France who really understood Gerhardt, and he was Laurent. Gerhardt had hitherto restricted himself in applying his two-volume theory to compounds alone; Laurent went a step further, and showed that the same theory must apply equally to elements. If, as Gerhardt had shown in so many instances, the number of atoms of hydrogen and chlorine—the one or other, or both together—present in a compound molecule was always a multiple of two, the same must apply to the elementary atoms themselves; the formula for hydrogen must be H_2 , for chlorine Cl_2 , symbolizing the weights present in two volumes. Here, as Laurent allowed, was a resuscitation of the bygone theory of Ampère. Gerhardt's atom, then, represented the smallest quantity of a simple body that could exist in a compound, while Laurent's molecule was the smallest quantity that could be employed in chemical reaction, a quantity divisible by two through the act of combination. The volumetric relations of hydrogen to chlorine, and of the mixed gases to the hydrochloric acid produced on their combination, thus found an easy explanation in the equation $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$; such equations, too, as $\text{N}_2 + 3\text{H}_2 = 2\text{NH}_3$, $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ similarly followed, and reconciled conflicting opinion, while the cause and character of the increased activity of substances in the so-called nascent state became at the same time apparent. Laurent¹ rebuked Gerhardt for speaking of atoms and equivalents as synonymous terms. Rightly he laid great stress on a true understanding of the meaning of chemical equivalence. Apart from the fallacy of admitting such formulæ as H_2O , Ag_2O

Laurent applies the two-volume theory to the elements, distinguishing atom, molecule, and equivalent.

¹ Laurent, *Chemical Method*, p. 9, *et seq.*

into a system based on a real equivalent notation, there was the question of $O = 8$, $S = 16$, $C = 3$, being taken as the equivalent of $H = 1$. If equivalence meant anything at all, surely it meant equivalence of function, and surely no one could speak of 8 parts of oxygen, 16 parts of sulphur, or 3 parts of carbon as taking over the functions of 1 part of hydrogen. Those quantities of chlorine, bromine, or iodine which replaced one part of hydrogen without affecting the general properties of the compound might be regarded as indeed equivalent, and similarly those quantities of metal which replaced one part of hydrogen in an acid. Some elements—manganese, for example—must be taken as possessing three equivalents.

Gerhardt's, Laurent's, both were voices as of those crying in the wilderness. To have accepted Gerhardt's two-volume theory would have meant repudiation of the honoured ether theories of Dumas and Liebig. Laurent's atoms, his molecules, his equivalents, his whole philosophy was so different from that of Berzelius, on whose name all men called, while his atomic system they decried. For many years yet the old system or want of system was the right system, the old formulæ the right formulæ. But slowly there came evidence from without that Gerhardt's and Laurent's formulæ were some of them, after all, right; then, that most were right; finally, that all must be right. Yet in 1856, when Gerhardt published his *Treatise*, it was only in the theoretical part of the work that he ventured to employ his new atomic values. In 1860, at the Karlsruhe meeting, Dumas could still maintain there were two chemistries, the one inorganic, the other organic, each with its own system of notation.

CHAPTER X

GERHARDT'S UNITARY SYSTEM

THERE are, I believe, chemists who hold that the history of their science has merely academic interest, is a study to be relegated to the library of the amateur or superannuated master, has not, and cannot have, any value to the present-day right-minded student of the living science. These only look forward, they have not time to look backward. To them the tale of progress is often the tale of unenlightened striving after truths which now appear axiomatic, the tale of wasted energy. Yet are these human. Many of them have interests to defend of vital importance to chemistry, and some will one day attain to that patronage which will allow of their doing lasting good or lasting harm to the science they have at heart, while others have already given up hope, pursued by hostile criticism, or broken by contemptuous neglect. For younger men in particular, for older men in particular, should the following paragraphs have value. They may give new life to the latter, and a sense of fresh opportunities to the former.

During the fourth decade of last century there raged a battle in the chemical world, whose outcome was the establishment of our science on that line along which it has so rapidly travelled up to the present, from the elementary atom to its most complicated compound. A great combat it was with the united weight of established opinion on the one side, and but two devoted beings on the other, two whose comparative youth and impoverished means elicited only contempt from the many,

while their striking originality evoked passionate repression from the few who could comprehend its existence. Pitiful were the circumstances to which those rebellious young Frenchmen, Laurent and Gerhardt, were reduced by the short-sighted, and in some cases envious, harshness of their scientific overlords; heroic their steadfastness when, as often, with scarce a sou between them to furnish the weapons of laboratory démonstration, they continued to oppose their philosophic convictions to the onslaught of highly-placed prejudice; glorious their victory, though proclaimed only after the miserable death of the one and the material exhaustion of the other. It was the enfranchisement of youthful opinion they won. From thenceforth established opinion might sometimes be wrong, respectable authority might not always be right. Theirs was the spirit that wins great victories. With their experimental evidence contemptuously denied, their persons vilified, their intellects disdained, they continued to work content in the belief that truth must ultimately prevail. The Parisian coterie, and this included those honoured names Gay Lussac, Thenard, Chevreul, and Dumas, proved a stubborn step-mother; but at last, when the very stranger cried shame, the elder of the two votaries, Gerhardt, was enabled to spend the last year of his life in receipt of a moderate competence.

Auguste Laurent¹ was born at La Folie, near Langres, on November 14, 1807. He was early destined to the parental occupation of wine merchant, but his loathing of the business routine, and his marked inclination towards scientific pursuits, decided his father to send him to Paris to study in the School of Mines. After his two years there he was appointed chemist to the manufactory at Sèvres, the uncongenial duties of which, however, soon drove him back to Paris to find independence in a garret. Here he received pupils and laid by a little money. But Laurent's end was science, not self, so he dismissed his school, and worked night and day till his savings were exhausted. Then he reopened his laboratory, financed

¹ Cf. Col. Yorke, *Quart. Jour. Chem. Soc.*, 7, pp. 149-157.

himself once more, and once more dismissed his students. He next accepted the position of chemist to a perfumer, which did not prevent him, however, being ready after two years with a theory of organic combination. This he submitted to the Faculty of Science in 1837, and was made doctor. After another year spent partly with the perfumer, and partly as chemist to a porcelain manufactory at Luxembourg, he was called to the chair of chemistry at Bordeaux. Eight years he remained there, ever contending with the limitations of his miserably furnished laboratory, and depressed by a sense of unrewarded merit, and by a feeling of purposed banishment from the capital as a scientific revolutionary. Laurent had meanwhile become acquainted with Gerhardt. The similarity of their views had soon caused this acquaintance to ripen into the most loyal and warm friendship. The thought of working side by side with Gerhardt it was which brought Laurent, in 1846, to Paris. But Paris did not want such firebrands as Laurent. Its scientific luminaries had been sufficiently displeased at his originality even before the association with Gerhardt. Still, proprieties had to be observed, so after two years, two years of dismal poverty and heartbreaking disappointment, he, being amongst the most brilliant of European chemists, was made an assayer to the mint. Here was bread and butter, though no laboratory. Though his means were slender, he yet could find something to fit up as a laboratory, a damp and unwholesome cellar in a corner of the mint, and energy there to utilize all the material he could afford—his chlorine, his ammonia, his sulphuric acid and potash; his water, alcohol, ether, and goniometer. He gave his means, he gave his life, for the demon of phthisis soon found him and slew him. Laurent died in 1853. "His interment was indeed sad," wrote Gerhardt; "twenty or thirty people only, and not a word on his tomb."

Just as the name of Liebig is indissolubly connected with that of Wöhler, so is that of Laurent with Gerhardt. "The great figure of Gerhardt," wrote Wurtz, "must not be separated from

that of Laurent; their work was collective, their talents complementary, their influence reciprocal. Equally potent in the vigour and profundity of their conceptions, the one (Laurent) exhibited unparalleled skill in the art of experiment, while the other shone pre-eminent through his method, the extraordinary appositeness of his views, and, above all, the compelling clearness of his exposition."

* Charles Frederic Gerhardt¹ was born at Strasburg in 1816. Destined, like Laurent, to a business career, his soul early rebelled. He had been sent to Leipzig to learn business; instead, he had acquired an overpowering love for science. He strove to subordinate his heart's desire to his father's wishes, but in vain. He left his home, and at nineteen years enlisted in a cavalry regiment. This life soon proved unbearable, and he was contemplating some headstrong action, when a German friend—it was Liebig—sent him money to purchase release. He was now able to seek his patron in Giessen, where he stayed eighteen months. In 1838 we find him in Paris, and three years later at Montpellier, to the university of which he had been nominated as Professor of Chemistry. His début in Paris had been most promising, but it was not long before a warning voice had come from Giessen as to the danger of stepping beyond the limits of experiment into the controversial land of theory, sacred to the comparatively old or very powerful. Like Laurent at Bordeaux, Gerhardt at Montpellier felt himself wasted. A miserably appointed laboratory, utterly uncongenial society, and a sense of designed ostracism, brought him after seven years to throw up his appointment and risk a return to Paris. Meanwhile, by his collaboration with Laurent in the publication of their *Comptes Rendus*, Gerhardt's popularity at home had certainly not increased, and for the seven years succeeding his return to Paris in 1848 he had to support himself by conducting a school for practical chemistry. Gerhardt's discovery of the acid anhydrides in 1852, and the success of his *Traité de Chimie Organique*, which was almost immediately translated into German and English, finally brought

Cf. Gerhardt and Grimaux, Vie de Gerhardt.

him reward, and in the January of 1855 he was offered, and accepted, the double chair of chemistry and pharmacy in his native town of Strasburg. At last he had a well-furnished laboratory, an honorific position, and a competence. The next year he died. "Yes, yes," cried Gerhardt on his death-bed, "in fifty years they will find I have done something. . . . I have advanced chemistry fifty years." He was buried with all honour. Impulsive as was Gerhardt, his attitude under the grossest attacks was æsthetically faultless, though his devouring love of truth rendered him blind to the need for circumspection. It was long before his "It is false" changed to "I hardly think it true." His honour as a man of science was spotless; his friendships warm and lasting.

The reader is in possession of that all-important part of Gerhardt's philosophy which gave him a constant standard by which to estimate the molecular magnitudes of those substances it was his life's aim to systematize. Yet if he would enter entirely into Gerhardt's mind, let him ever remember that the new chemistry was to be one cleared of all hypothesis or preconceived opinion, one with a language symptomatic of neither radicals nor dualism, but expressive rather of honest if crude empiricism. The anomaly¹ of one substance, alcohol, having such different formulæ as the $C_4H_8 + H_4O_2$ of Dumas, the $(C_2H_6)O$ of Berzelius, the $C_4H_{10}O + H_2O$ of Liebig, the $C_4H_{10}O_2 + H_2$ of Zeise and Mitscherlich, was to disappear before the one formula, the formula of the unitary system, C_2H_6O . In reading what follows, too, he must keep before his mind the fact that Gerhardt and Laurent had a test of the legitimacy of their empirical formulæ in the divisibility of the number of the hydrogen, chlorine, and nitrogen atoms—dyads, Laurent called them—by two. It was an empirical law, but one deserving of consideration, for ultimately it brought us a step nearer a sense of valency, and immediately it led to the correction of many formulæ hitherto accepted; among others of butyric acid,²

The basis of Gerhardt's scheme of formulation.

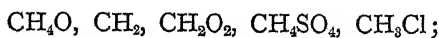
¹ Gerhardt, *Précis de Chim. Org.*, p. 10.

² Cf. Kopp, *Entwicklung der Chemie*, pp. 734, 741.

written $C_3H_7O_4$, and glycocoll, $C_2H_5N_2O_7$; also to the refusal of others apparently self-evident, of CH_3 and C_2H_5 for the uncombined methyl and ethyl radicals.

Gerhardt's
ladder of
combustion.
Homology.

It was in 1841¹ that Gerhardt entered on a research to discover some general law which might suggest an all-sufficing system of classification, and the following year he was ready with his "ladder of combustion"—with its highest rung cerebral matter, its lowest carbonic acid, water, and ammonia—to enfold the whole science of organic chemistry. He soon found, however, that this arrangement, according to mere complexity of composition,² was no sufficient classification, so he betook himself to another line of enquiry. A note of triumph seems to ring through the following lines from the preface to his *Précis de Chimie Organique*,³ published in 1844: "I have succeeded in establishing homologous series. . . . These have indicated to me the means of classifying organic substances in natural families, and of disposing them on a kind of combustion ladder." As a matter of fact, it was only the word "homology" that Gerhardt could claim as his own. Two years earlier Schiel⁴ had shown that a very simple relation existed between the alcohols then known, that their radicals might all be represented by the general expression $nR + H$, R suggesting the group $C_2H_2(C = 6)$; moreover, in the same year Dumas had demonstrated the existence of a similar relation between the several members of the fatty acids known to him. Yet the merit of generalizing from this fact of homology, of demonstrating the possibility, nay the necessity, of prophesying the existence of terms yet unknown in his series, their physical and chemical properties, is Gerhardt's alone. And so in 1848 Gerhardt could with decision take as a lower rung of his ladder the series⁵—



¹ *Vie de Gerhardt*, p. 317.

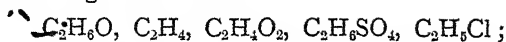
² *Ibid.*, p. 318.

³ p. x.

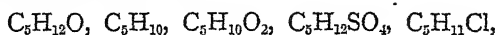
⁴ Cf. Kekulé, *Lehrbuch*, i., 37.

⁵ Gerhardt, *Introduction à la Chimie*, p. 291.

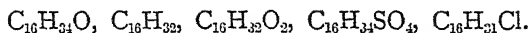
as the next higher the series—



and at intervals the series—



and—



The aromatic bodies, too, benzene and cumene, for example, had series related to them which took place in his all-containing combustion ladder. By no means few were the series of hydrocarbons, aldehydes, and acids which he could call homologous, and which he advanced in vindication of his system. Yet there were several notable lacunæ, those to be filled by the substances C_3H_8 , C_7H_{14} , $\text{C}_{11}\text{H}_{22}$ among the hydrocarbons, $\text{C}_6\text{H}_{12}\text{O}$, $\text{C}_8\text{H}_{16}\text{O}$, $\text{C}_9\text{H}_{18}\text{O}$ among the aldehydes, $\text{C}_{13}\text{H}_{26}\text{O}_2$ among the acids. But, as Gerhardt said, "It suffices to know the chemical history of one single term in a homologous series to deduce *a priori* the history of all the rest." It was only when he came to the highest rungs of all, those formed by the proteid substances, fibrin, albumin, casein—"the most complex of organic combinations"—that he was unable to seriate with so nice a sense of propriety. He could only place them tentatively by the light of a knowledge of many well-known compounds produced by their putrefaction or oxidation. Refreshing it is to read Gerhardt's writings. One feels the master mind, the mind with a real grip of essentials. Their immediate effect on his countrymen may be judged by a perusal of the first few pages of Regnault's *Précis de Chimie Organique*,¹ published in the very early fifties: their theme is the natural history of wood, cellulose, and starch.

But we must leave Gerhardt a while to consider three series of investigations of all importance as offering experimental basis to the next advance of chemical theory. The investigations referred to are those of Hofmann and Wurtz on the

¹ Cf. *Vie de Gerhardt*, p. 241.

compound ammonias, of Williamson on the constitution of the ethers, and of Frankland and Kolbe on the isozation of the organic radicals. Here was work achieved which gave command to chemists over three of the most obstinate provinces within their ken; work carried through during the short space of four years, which alone would render enduringly famous the otherwise famous names of Hofmann and Wurtz, Williamson, Frankland and Kolbe.

Wurtz and
the com-
pound
ammonias.

In 1849 Wurtz¹ made the discovery that on boiling the ethereal salts of cyanic or cyanuric acid with potash, gases were evolved which, while possessing most of the properties of ammonia, were yet different from ammonia in that there was present in their molecule a considerable percentage of carbon. They were, in fact, members of that fast accumulating group of substances called organic bases. Ten years earlier Liebig had concluded that amides—a class of bodies whose existence was first recognized after Dumas' discovery of oxamide in 1830—owed their specific properties to the presence in them of the radical NH_2 , and looked forward to the time when such a compound as $\text{H}_2\text{N.C}_4\text{H}_5$ or Ad—Ae, certainly having the properties of ammonia, should become the possession of chemists. Berzelius saw in every organic base a particularly well-defined example of the copulation of passive hydrocarbon or anhydrous acid with active ammonia. Hofmann, in 1848, was inclined to accept this explanation of the constitution of aniline, but then he discovered that while some ammonium salts lost four atoms of hydrogen as water when treated with phosphorus pentoxide, the corresponding aniline salts were carbonized; it was unlikely, therefore, that the latter contained the group $\text{NH}_3.\text{HO}$ or any saline derivative. And now Wurtz' new series of compound ammonias, each member of which behaved in a manner entirely analogous, and Hofmann's² own discovery, that the same bodies might readily be obtained by treating ethyl bromide, etc., with

¹ *Ann. Chim. Phys.*, 30 (1850), p. 443.

² *Ann. Chem. Pharm.*, 74, p. 116.

aqueous or alcoholic ammonia, seemed to show clearly that these organic bases did contain Liebig's amide radical, and were produced by the simple exchange of one hydrogen atom of ammonia for the hydrocarbon radical of the bromide employed. There was no reason to expect an elimination of four hydrogen atoms from a body $X.NH_2.HO$, or to demand a more complicated equation than $X.Cl + H.HN_3 = X.NH_2 + HCl$, to explain his reaction.

It was not in Liebig's sense, however, that Hofmann accepted the amide radical. If, as seemed to him probable, aniline was a body of the type $N \begin{Bmatrix} H \\ H \\ X \end{Bmatrix}$, there seemed every reason

Hofmann seeks and finds bi- and tri-substituted ammonias.

to suppose that other substances of the general type $N \begin{Bmatrix} H \\ X \\ X \end{Bmatrix}$ and

$N \begin{Bmatrix} X \\ X \\ X \end{Bmatrix}$ might be produced from the same ammonia. In turn he

tried the effect of heating aniline with phenol and chlor-benzene. Failing in his design, he then heated aniline with ethyl bromide; he thus obtained beautiful crystals of a substance with the formula $C_{16}H_{11}.N.HBr$, from which, by the action of potash, was separated a clear liquid with the composition $C_{16}H_{11}N$, which formed a hydrochloride $C_{16}H_{11}.N.HCl$, which again with platinum chloride formed a double salt $C_{16}H_{11}N.HCl.PtCl_2$. Further addition of ethyl bromide to the base so produced resulted in the isolation of a body $C_{20}H_{15}.N$ with again a chloride and again a platinum double salt. There could be little doubt that here were indeed the substances he

sought of the types $N \begin{Bmatrix} H \\ X \\ X \end{Bmatrix}$ and $N \begin{Bmatrix} X \\ X \\ X \end{Bmatrix}$ respectively, viz. $\left. \begin{matrix} C_{12}H_5 \\ C_4H_5 \end{matrix} \right\} N$

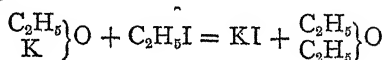
and $\left. \begin{matrix} C_{12}H_5 \\ C_4H_5 \end{matrix} \right\} N$, and when, substituting amyl bromide for ethyl

bromide in the second reaction, he obtained a body $\left. \begin{matrix} C_{12}H_5 \\ C_4H_5 \\ C_{10}H_{11} \end{matrix} \right\} N$,

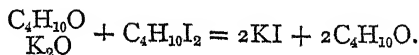
and again, and this time by the direct action of ammonia, the bases mono-, di-, and tri-ethylamine, each retaining in their entirety the basic properties of ammonia and its power of forming a double platinum salt, all doubt vanished. And might one not now regard the body C_6H_5P , recently discovered by Paul Thenard, as a tri-methyl phosphine! Whatever view was taken of the inner constitution of all these new substances, one thing was certain, and both Hofmann and Wurtz laid stress upon it, a homologous relationship obtained among them.

William-
son's work
on the
ethers.

At the time when Williamson¹ published his theory of etherification there were three theories of the relationship between alcohol and ether prevalent; the first that of Berzelius, who regarded these two substances as oxides of quite different radicals, $(C_4H_5)O$ and C_2H_5O ; the second based on Dumas' etherin theory, that both were hydrates of the same radical etherin C_4H_4 , formulated $C_4H_4.H_2O$ and $2C_4H_4.H_2O$ respectively; the third and most popular that of Liebig, who conceived alcohol $C_4H_5.H_2O$ as the hydrate of ether C_4H_5O . Now Williamson found that if the body produced by the action of metallic potassium on alcohol were mixed with ethyl iodide, ordinary ether was produced. The reaction might be expressed by two equations irreconcilable with each other, but quite consistent respectively with the views of the constitution of alcohol and ether taken by Berzelius and Liebig—



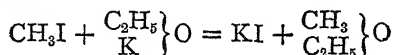
and—



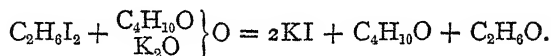
When, however, methyl iodide was substituted for ethyl iodide, a volatile substance was produced, which, on combustion in Liebig's apparatus, proved to have the formula C_3H_5O .

¹ *Quart. Jour. Chem. Soc.*, 1852.

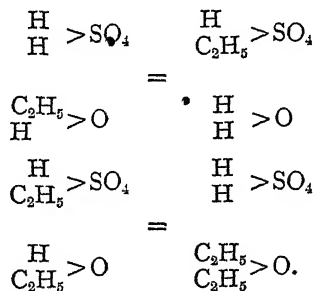
There were traces neither of ether nor methyl oxide. It was easy, then, to choose between the following equations—



and—



Here was victory for Gerhardt's two-volume theory; for the formulæ $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{H} \end{array} \right\} \text{O}$ and $\left. \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{O}$ both represented two volumes of vapour; and indeed Williamson employed Laurent and Gerhardt's notation throughout his paper. The course of etherification, too, as ordinarily carried on, was now clear, and was denoted thus by Williamson:—



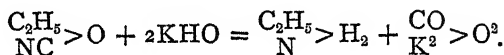
The continuous formation and decomposition of the sulphovinic acid he was able to demonstrate by adding amyl alcohol towards the end of his experiment, and so obtaining sulphoamyllic acid.

Williamson laid great stress on the substitution of hydrogen atoms by the ethyl radical. He took the water molecule as the type of all alcohols and ethers; and though in this he showed no particular originality—for Laurent¹ had taken precisely the same attitude in 1846, while later the American, Sterry Hunt, had shown how capable of development the idea was—he has

The water-type.

¹ *Ann. Chim. Phys.* 18, p. 266.

the merit of its physical demonstration and of suggesting the many other and more complicated substances whose proximate composition is revealed by reference to this same water type. Thus acetic acid might be written $\text{C}_2\text{H}_3\text{O}\left\{\begin{smallmatrix} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{smallmatrix}\right\}\text{O}$; and on the analogy of the ether molecule one might even suspect the existence of a body with the formula $\text{C}_2\text{H}_3\text{O}\left\{\begin{smallmatrix} \text{C}_2\text{H}_3\text{O} \\ \text{C}_2\text{H}_3\text{O} \end{smallmatrix}\right\}\text{O}$. As time passed, Williamson became possessed by this idea of referring the constitution of substances to that of water. Certainly all inorganic compounds, and indeed the bulk of the best-known organic substances, thus received their suitable presentment. True, in some cases—those of the dibasic acids, for example—the typical substance had necessarily its formula doubled, sulphuric acid, $\text{SO}_2\left\{\begin{smallmatrix} \text{SO}_2 \\ \text{H} \end{smallmatrix}\right\}\text{O}_2$, being made akin to $\text{H}_2\left\{\begin{smallmatrix} \text{H}_2 \\ \text{H}_2 \end{smallmatrix}\right\}\text{O}_2$; and in others replacement of the typical oxygen was deemed possible, as when ethylamine was produced by the action of potash on ethyl cyanate, for instance—



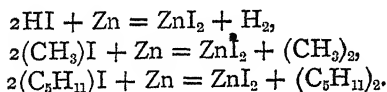
But in these exaggerations there were elements of truth which could not but exert a healthy influence on the subsequent development of chemical science.

Frankland and Kolbe discover the free hydrocarbon radicals.

Years before, in 1834, when his head was full of his new radical theory, Liebig had foreseen the possibility of obtaining his radical C_4H_{10} in the free state, and, mindful of Bunsen's experiments on cacodyl, he had even suggested the action of potassium on ethylic chloride or bromide as likely to produce the desired substance. This experiment had been tried four years later by Löwig without success, and interest in the question of free radicals had then waned. In 1848 Frankland¹ and Kolbe, working in Bunsen's laboratory at Marburg, and with Löwig's ill-success before their minds, investigated

¹ *J. C. S.*, 1, p. 60; *ibid.*, 2, p. 263.

action of potassium this time on ethyl cyanide. In vain. There was certainly a gas evolved, but analysis showed it to be ethylic hydride with no trace of the free radical. The next year Frankland tried again. If, as experiment suggested, the equation $2\text{C}_2\text{H}_5\text{I} + \text{K}_2 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + 2\text{KI}$ adequately represented the action of potassium on ethylic iodide, it might well be the violence of the reaction that caused disruption of free ethyl. Were a less positive metal—say zinc—chosen, the result might be very different. Experiment justified his belief, and he so obtained specimens of pure ethyl and amyl. For the moment the nature of Frankland's reaction seemed obvious. He had before his mind the proved constitution of ether, the progressive substitution of hydrogen atoms in ammonia by hydrocarbon radicals, Laurent's convincing doctrine of the two-atom molecule of hydrogen. The truth of one of the following equations stood or fell with the truth of the others:—



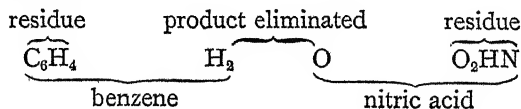
Soon, however, he was seized with doubts. Here were no free radicals at all. It was with the radical hydrogen, H , not with the compound molecule of hydrogen, H_2 , that he must compare free methyl, ethyl, or amyl. If, again, free methyl possessed the composition $(\text{C}_2\text{H}_3)_2$, how could he explain the production from it of bodies with the empirical formulæ $\text{C}_4\text{H}_5\text{Cl}$ and $\text{C}_4\text{H}_4\text{Cl}_2$ on the successive addition of chlorine—bodies having clearly the constitution $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2\text{Cl}$ and $2\text{C}_2\text{H}_2\text{Cl}$? On the other hand, the hydrocarbons C_2H_4 , C_4H_6 , admittedly occupying two volumes in a state of vapour, readily yielded the products $\text{C}_2\text{H}_3\text{Cl}$ and $\text{C}_4\text{H}_5\text{Cl}$, likewise occupying two volumes. Frankland, and with him Kolbe, felt themselves committed to this—that there were two quite distinct homologous series of hydrocarbons isomeric with each other, viz.—

Methyl, C_2H_3 ; methyl hydride, C_2H_3H .
 Ethyl, C_4H_5 ; ethyl hydride, C_4H_5H .
 Propyl, C_6H_7 ; propyl hydride, C_6H_7H .
 Butyl, C_8H_9 ; butyl hydride, C_8H_9H .
 Amyl, $C_{10}H_{11}$; amyl hydride, $C_{10}H_{11}H$.

Seldom have we found in the history of chemistry the dominance of one idea productive of such reasonable perverse reasoning. Frankland's reversion, on second thoughts, to equivalent formulæ is interesting.

Gerhardt's
theory of
residues.

The idea of accepting empirical formulæ as the limit to philosophic investigation was not originally Gerhardt's, for Baudrimont,¹ in 1838, had boldly stated that a compound in its last state of division must be regarded as a complex of atoms bound each to all and all to each. As we have seen, it was in accordance with this principle that Gerhardt had composed his combustion ladder. But Gerhardt was too broad-minded a student to be ridden by a principle which, after all, might only be of the nature of an expedient; and sworn foe as he was of the radical, he could not but admit that certain groups of atoms did continually recur in chemical substances. He found reconciliation between his principle and experience in his theory of residues. All chemical change being the result of a double decomposition, there must remain, say, on the elimination of water through the action of benzene² on nitric acid, that part of the benzene molecule, which was hitherto combined with the hydrogen of the water, and that part of the nitric acid hitherto combined with the oxygen. It was these two remainders, "residues," which combined to form nitrobenzene. So—



¹ Gerhardt, *Précis de Chim. Org.*, p. 10.

² *Ibid.*, p. 65.

Here were two facts, and the one implied the other, combination through double decomposition and the affinity of residues; these facts and the occurrence of substitution, when one element was not only replaced but had its functions fulfilled by another element, Gerhardt came to regard as the foundations of organic chemistry.

To express a combination of residues Gerhardt employed the term copulation, not at all, however, in the sense in which he had used it in 1839. His copulæ were now his residues, his copulated compounds such as were formed from two others with elimination of water. In 1853 he introduced the idea of copulated radicals—he afterwards called them conjugated radicals—radicals formed from simpler residues, which were his earlier copulæ and now his constituent radicals, radicals capable of forming compounds analogous to those of simpler residues, such complexes, for example, as $C_6H_5SO_2$ and $C_7H_4(NO_2)O$.

Gerhardt's
copulated
radicals.

The discoveries of Williamson, Frankland, Kolbe, Wurtz, and Hofmann only made Gerhardt the more certain of his having rightly conceived the meaning of double decomposition, of residual reaction. He was therefore quite in a position to grasp the facts and their inner meaning, more so, indeed, than their authors, with their attention focussed on the one particular series that had come under their notice. The unitary system¹, of which he felt himself the author, was sufficiently comprehensive for all. Under this system all substances were considered as molecular entities, in which the atoms were disposed in a determined order, an order, however, only indicated relatively by their chemical metamorphoses. Formulæ could indeed give the sense of only one or two reactions, never the true image of molecular constitution. And in this sense Gerhardt gladly accepted Williamson's view of the constitution of alcohol and ether; ether was really a product of the decomposition of alcohol, and the relation between the two was adequately expressed by their formulæ $C_2H_5\left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right\} O$ and

The
unitary
system
covers all
contem-
porary dis-
covery.
Gerhardt
prepares
the acid
anhydro-
drides, and
produces
his
*Traité de
Chimie.*

¹ Cf. *Vie de Gerhardt*, p. 362.

$\left. \begin{matrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix} \right\} \text{O}$. He himself now wrote $\frac{\text{NO}_2}{\text{NO}_2} > \text{O}$ as the formula for Deville's nitric anhydride, and $\left. \begin{matrix} \text{C}_7\text{H}_5\text{O} \\ \text{C}_7\text{H}_5\text{O} \end{matrix} \right\} \text{O}$ as suitably formulating the hypothetical anhydride of benzoic acid. Imagine his delight when, in 1852, after heating equivalent quantities of benzoyl chloride and potassium benzoate, he obtained a beautifully crystallized body, which with water produced benzoic acid, with alcohol ethyl benzoate, with ammonia benzamide, and which could then only have this very formula $\left. \begin{matrix} \text{C}_7\text{H}_5\text{O} \\ \text{C}_7\text{H}_5\text{O} \end{matrix} \right\} \text{O}$! Liebig's¹ comment on this is instructive.

"The discovery of the anhydrides of organic acids is one of the most brilliant that has been made of late. It is strange that the two theories [the unitary and the radical] hitherto opposed should have led to one which explains all the phenomena in their two senses." Williamson speaks of a new day having dawned on the constitution of acids and salts, and one thinks of old Berzelius' comment on the birth of benzoyl. Even in France Gerhardt found tardy recognition, and was offered the completion of the French edition of Berzelius' text-book. But Berzelius edited by Gerhardt! The thing was impossible, so there came into being the *Traité de Chimie Organique*. But it was only in the fourth and final volume of his great work that Gerhardt pronounced his views in their final development. When asked why, in his first three volumes he had retained the equivalents of Gmelin with the barred symbols of Berzelius, he had laughingly answered, "otherwise no one would have bought my book." Throughout, however, the new light which had fallen upon him illuminates its pages. He had discovered a constant basis for the subdivision, into four classes, of each group of each homologous series that formed the successive rungs of his combustion ladder of 1848, classes differentiated by marked chemical dissimilarity, and with each a prototype in the inorganic world. His acetic series² included eight groups,

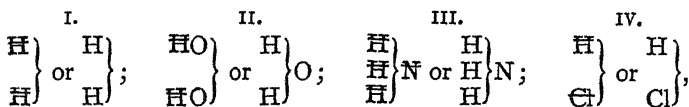
¹ Cf. *Vie de Gerhardt*, p. 403. ² Gerhardt, *Traité de Chim.*, Org. i. p. 552.

the first of which—the group methylic—was composed of the following among others :—

		Volume I		Volume IV	
		Type		Type	
Methylene	C_2H_2	—	—	—	—
Methyl	C_2H_6	$\left\{ \begin{array}{c} Me \\ Me \end{array} \right\}$	$\left\{ \begin{array}{c} H \\ H \end{array} \right\}$	—	—
Methyl hydrate	$C_2H_4O_2$	$\left\{ \begin{array}{c} MeO \\ HO \end{array} \right\}$	$\left\{ \begin{array}{c} HO \\ HO \end{array} \right\}$	$\left\{ \begin{array}{c} Me \\ H \end{array} \right\} O$	$\left\{ \begin{array}{c} H \\ H \end{array} \right\} O$
Methyl sulphhydrate	$C_2H_4S_2$	$\left\{ \begin{array}{c} MeS \\ MeO \end{array} \right\}$	—	$\left\{ \begin{array}{c} Me \\ H \end{array} \right\} S$	—
Methyl chloride	C_2H_3Cl	$\left\{ \begin{array}{c} Me \\ Cl \end{array} \right\}$	$\left\{ \begin{array}{c} H \\ Cl \end{array} \right\}$	$\left\{ \begin{array}{c} Me \\ Cl \end{array} \right\}$	$\left\{ \begin{array}{c} H \\ Cl \end{array} \right\}$
Methyl ammonia	C_2H_3N	$\left\{ \begin{array}{c} Me \\ H \\ H \end{array} \right\} N$	$\left\{ \begin{array}{c} H \\ H \\ H \end{array} \right\} N$	$\left\{ \begin{array}{c} Me \\ H \\ H \end{array} \right\} N$	$\left\{ \begin{array}{c} H \\ H \\ H \end{array} \right\} N$
Methyl phosphide	C_2H_3P	$\left\{ \begin{array}{c} Me \\ Me \\ Me \end{array} \right\} P$	—	$\left\{ \begin{array}{c} Me \\ Me \\ Me \end{array} \right\} P$	—

These are but a few of the compounds enumerated in the methyl group; all, however, fall under one or other of the types—

Gerhardt's classification by types.



types which, to use his word, must be regarded as the “jalon” of the series. In Gerhardt's opinion all future speculation was bound up in a complete understanding of these series, the ordering and furnishing of which could only come, however, with a determining of the laws according to which the properties of a given type are altered through substitution of some of its elements by other elements or groups of elements.

It will be remembered how Williamson, in his desire to discover all matter as built on his water type, had at times employed a reduplicated water molecule as the mother substance. So he had written sulphuric acid $\left\{ \begin{array}{c} SO^2 \\ H^2 \end{array} \right\} O^2$. Gerhardt

Gerhardt and poly-atomic radicals.

saw the value of this formulation, how clearly it differentiated between mono- and di-basic acids, and added, as the suitable general expression of a tribasic acid, the triple water type. He already knew that basicity depended on the number of hydrogen atoms replaceable in an acid; but that these one, two, or three hydrogen atoms were held together in the acid, he now saw to depend on the presence of some radical, for which he proposed the adjectives mono-, di-, or tri-atomic, according as it held bound one, two, or three of these hydrogen atoms.

And here we are at the zenith of Gerhardt's philosophy; we see how it was Gerhardt's mind which made general and fertile the brilliant yet isolated discoveries of Williamson, Hofmann, and Wurtz, his mind which could grasp the interrelation of their several interpretations of facts and bring together into one comprehensive scheme all the multitudinous substances of inorganic and organic nature, known or ever to be known. As this theory of types stood at Gerhardt's death, so it stands to-day, though disembarassed of that suspicion which must always attend the inception of an all-embracing generalization. While one sorrows over Gerhardt's untimely death, one yet feels that his life's work was done. His system of chemistry was as perfect as could be any system based otherwise than on an appreciation of the interplay of the individual atoms; and with his unimaginative and somewhat pragmatistical mind it seems improbable that he could ever have come to regard the atom as anything other than a mere number, that he could ever have conceived it as a physical entity with activities discernible by the human mind. I believe that Gerhardt brought a greater intellect to bear on chemical research than any of his contemporaries, save Berzelius, that both did accomplish their greatest, and that the fair fame of the former was only fortunate in being spared the shadow which post-meridian activity must always throw on the reputation of an experimental philosopher.

CHAPTER XI

VALENCY, THE CHEMICAL NATURE OF CARBON, AND THE CONSTITUTION OF ORGANIC COMPOUNDS

WE have now arrived at times of real prosperity for chemical science, times when laboratories were erected in each of the more prosperous centres of Western European life, laboratories whose doors were opened to any who desired to work. Among the ever-increasing number of enthusiasts whose heads and hands contributed to the making of the present-day chemistry, we will speak more intimately of those whose work marked out the line of advance by enriching the science with new general truths and ideals. The pure chemists of the latest epoch to whom organic chemistry owes most are Frankland, Kolbe, and Kekulé.

Edward Frankland¹ was born at Churchtown, near Lancaster, in 1825. He very early showed signs of intelligent and practical interest in natural phenomena, and his parents were desirous of his pursuing the medical profession. After consulting ways and means, however, they found that the only road open was through the druggist's shop, so for five years the boy was consigned to the care of a local tradesman, from whom he learnt the finesse of the mortar, and a facility in making parcels. Then his enfranchisement came, for his quick intelligence had aroused interest in certain local magnates, who brought about his entrance to Playfair's laboratory in London. Here he met Hermann Kolbe, with whom he

Frank-
land,
1825-
1899.

¹ Cf. *Sketches from the Life of Sir Edward Frankland*.

travelled to Marburg in 1847, to work in Bunsen's laboratory. These were the days when Liebig was attracting all to Giessen, and there went Frankland in the winter of 1849-50. Liebig was not slow to recognize his pupil's gifts, and his energetic word had much to do in the election of Frankland the following year to the chemical chair at the recently founded Owens College, Manchester. But Frankland found the work in Manchester uncongenial, and in 1857 returned to London as Professor of Chemistry at St. Bartholomew's Hospital. Frankland's name was now great in scientific circles, and his next step was to the chair at the Royal Institution, vacated by Faraday in 1863. Here he found real satisfaction: no laboratory teaching in which he had no interest, some lecturing which pleased him, and much time for his own investigations. Later, Frankland succeeded Hofmann at the Royal College of Chemistry. Frankland died in 1899 while on a visit to Norway, having lived to see the fruits of his labours blessed scientifically and honorifically in the highest degree. Through long years he stood for English chemistry, eminent as a pioneer in the pure science, and at home continually called in to advise in the commercial interest. He was knighted (K.C.B.) on the occasion of Queen Victoria's diamond jubilee, having been already worthily recognized by most of the learned societies at home and abroad. A full man was Frankland; with his love of music and delight in travel, with his garden, his observatory, and his workshop, he was busy to the last, and very warm tributes of respect, affection, and almost veneration followed him to the grave. In years to come he will rank as a chemist with almost the highest.

Hermann Kolbe¹ was born at Elliehausen, near the university town of Göttingen, in the year 1818. At the age of fourteen he entered the Göttingen Gymnasium, where he remained till 1838, when he became a student of chemistry under Wöhler, who occupied the professorial chair. It was during his last year in the Gymnasium, and through the

¹ Cf. E. Meyer, *Zur Erinnerung an Hermann Kolbe*.

conversation of a schoolfellow, a common friend of himself and Bunsen, then a "privatdocent" in the university, that Kolbe first had his thoughts turned to the subject his life was so brightly to illuminate. In 1842 he went to Marburg to assist Bunsen, who had been made ordinary professor that same year; and in 1843 he was made Doctor. Kolbe, while with Bunsen, had naturally acquired his master's method of gas analysis. Playfair in London was engaged on an investigation of atmospheric air, and Kolbe was invited to assist him. So to London he came in 1845. The two years Kolbe spent in London were most profitable to chemistry. He was given every opportunity for research, and in the companionship of Frankland found an ever-potent stimulus. In 1847 Kolbe returned to Marburg, taking Frankland with him. The same year he was invited to Brunswick, where he stayed four years, editing Liebig and Wohler's text-book. He then, to his astonishment, received a call to Marburg to fill the chair left vacant by Bunsen's translation to Breslau. He was well chosen; his reputation as a teacher spread far and wide, and was scarcely eclipsed by that of Liebig. He had no longer to fight his battles single-handed. Through his advice, instruction, and practical assistance work was done in that laboratory at Marburg which gave formulation a new and fuller meaning. Honourably recognized and rightly appraised by Kolbe was the work done by his many pupils. In 1865 Kolbe was transferred to Leipzig, and in 1868 the new laboratory promised him was ready for occupation, an enduring monument to the broad-minded liberality of the state of Saxony. Kolbe died in 1884.

Kolbe was a chemist of Berzelius' school. He was consequently to the end of his life an uncompromising reactionary from the new school of Gerhardt and Kekulé. Berzelius, Liebig, Wöhler, and Bunsen! These were the real workers for chemistry. Gerhardt and Kekulé! While the types of the one he regarded as the most trivial and empty play on formulæ, the linked carbon theory of the other affected him with a nausea that drove him in controversy to unseemly

personalities. Kolbe was a stern disciplinarian. He had received his canon straight from Berzelius, and gave the whole of his practical, somewhat unimaginative, mind to its development. Without Berzelius there would have been no Kolbe, without Kolbe there would be little of the security we feel in our conception of the organic molecule. But in private life Kolbe was a very different man from the harsh, unbending critic of innovation known to the outer world. From the beginning of his career he drew to himself the friendship of the best, and with advancing years he won from his pupils almost filial veneration.

Kekulé,
1829-
1896.

Friedrich August Kekulé,¹ the son of a Hessian Oberkriegrath, was born at Darmstadt in 1829. It was intended that he should become an architect, and it was as a student of architecture that he joined Giessen University in 1847. But the spell of Liebig's enthusiasm soon held him fast, and he determined to be a chemist. In 1851 he travelled to Paris, and there heard Dumas lecture, and found the friendship of Gerhardt. After a year spent in Paris, and another in Switzerland, he came over to England to become Stenhouse's assistant, and was soon on terms of intimacy with Williamson and Odling. It is not surprising that after these varied experiences he could say, "I no longer belonged to any school." Kekulé remained two years in London, and then went to Heidelberg, to become a lecturer in the university there. In 1858 he was made Professor in the University of Ghent, and then followed nine years during which his productive powers were at their height. Before they had passed, he had established the philosophy of the linked carbon atom, he had laid the foundation of the chemistry of the aromatics by his doctrine of the carbon ring, and he had published his text-book. In 1869 he was called to the chemical chair at Bonn. Seven years after, Kekulé's physical powers began to fail. He had borne witness to the truth of his old master Liebig's saying, "A man who would be a chemist must be prepared to sacrifice

¹ Cf. *J. C. S., Memorial Lectures*, No. vii.

his health." Many were the nights through which Kekulé had toiled to acquire that subtle instinct by which he was led from the single carbon atom to its most complex derivative. Kekulé had the gift of imagination, great, for it was allied with an aptitude for hard and patient research. "Let us dream, gentlemen," said he; "perhaps we shall find the truth, but let us be silent till our vision has been put to the truth by the awakened understanding." Kolbe did great things; what might he not have done had he possessed this sacred gift?

Kekulé died in 1896, full of honours, ennobled by his sovereign, an esteemed member of most of the scientific societies of Europe, and with a fresh memory of the magnificent festival held but six years previously in honour of the twenty-fifth anniversary of the birth of his benzene formula. His impressive figure and extraordinary mind will be long remembered by his scientific posterity.

I have said in the previous chapter that the theory of types stands now as it stood when Gerhardt died in 1856. It stands for the vindication of what in its essence was Gerhardt's life-work, the recognition of a two-volume standard for molecular weights. Yet when one glances at Gerhardt's typical formulæ, one is momentarily led to consider that here at last was recognition, only waiting definite expression, of some limited saturation capacity of elementary atoms; for the fact that three

Neither Berzelius nor Gerhardt was in a position to recognize the valency of atoms.

types, $\begin{matrix} \text{H} & \text{H} \\ \text{H} & \text{H} \end{matrix} \left. \vphantom{\begin{matrix} \text{H} & \text{H} \\ \text{H} & \text{H} \end{matrix}} \right\} \text{O}, \begin{matrix} \text{H} \\ \text{H} \end{matrix} \left. \vphantom{\begin{matrix} \text{H} \\ \text{H} \end{matrix}} \right\} \text{N}$, are preserved in so many compounds,

must ultimately be dependent on the fact that the atoms H, O, and N have a predilection respectively for one, two, or three atoms of another element. But to understand precisely Gerhardt's attitude, one must remember, first, that atoms were to him mere numbers, expressive indeed of material units, but of units whose individual circumstances it was useless to inquire into; secondly, that his system was a unitary system, that is, an empirical system, finding expression in formulæ, each symbol in which might be regarded as signifying an atom

bound to each one in turn or all at once of the other atoms; and lastly, that he did in very fact at different times find quite different formulæ for the same substance most clearly expressive of its various metamorphoses. Even Berzelius, with his wonderful clearness of mental vision and powerful imagination, Berzelius, whose atomic system has now been accepted in its entirety, had never ventured on any suggestion of a limited or constant combining capacity of the atoms he knew so well. His dualistic theory, his belief, for example, that H_2O could as such combine with SO_3 , was partly accountable for this, and partly, too, the wideness of the field he worked. And so we have the two greatest minds that during the last century were occupied with chemistry, both blinded to the recognition of a principle of the last importance to the furtherance of their science, and one almost obvious to a youth bringing an unbiassed mind to bear on the results of a single investigation. With the gradual recognition of this principle, that each elementary atom possesses a definite combining capacity, there came recognition of what was good in Berzelius' philosophy, and understanding how came those structural phenomena generalized by Gerhardt. Gerhardt out of chaos had developed cosmos, and Frankland had given soul to the latter; yet this new creation was not immediately potent to convince. Liebig had been premature in extolling the combination through types of unitary with radical theory, for Kolbe during many years could fight Berzelius' battle of the "copulæ," in the light of the new doctrine of atomicity, as Kekulé could Gerhardt's battle of the types, and there was not wanting in either case argument, often convincing, that the adverse school was baseless and pernicious. In reading the following account of Kolbe's work, let it be understood that it was only in 1870 that he forsook Gmelin's equivalent values for carbon, oxygen, and sulphur, and that he did not accept the two-volume theory of Gerhardt as security for the right measurement of the molecule; also that for him formulæ were merely symbolic expressions of chemical ideas, and that to make these ideas as clear and far-reaching as possible was his life's work.

In 1843 Kolbe became doctor of science in the University of Marburg, presenting as his thesis an account of the action of chlorine gas on sulphide of carbon. He had discovered that the substitution of sulphur by chlorine took place by two stages, the substances CCl_2 and $\text{CS}_2 + \text{C}\text{Cl}_2$ being produced. The reaction continued to interest him, and in 1845 he tried the effect of moist chlorine on the same carbon sulphide. He obtained a substance with the formula $\text{C}\text{Cl}_2.\text{SO}_2$, from which, by the action of potash, was produced a salt $\text{KO} + \text{C}_2\text{Cl}_3.\text{S}_2\text{O}_5$. Kolbe had been brought up in the school of Berzelius, and therefore this employment of copulation formulæ seemed necessary; moreover, the marked analogy between his last new sulphur compound and trichlor-acetic acid, to which Berzelius had given the formula $\text{HO} + \text{C}_2\text{Cl}_3.\text{C}_2\text{O}_3$, struck him immediately. The fact published in the same paper that the compound CCl_2 , by further action of chlorine in presence of water, left a quantity of tri-chloracetic acid, was further reason why his mind should now turn to the solution of the vexed question of the composition of this and kindred acids. In 1847 Kolbe was working in Playfair's laboratory.¹ Edward Frankland, then aged twenty-two, was a fellow-assistant, and the two set themselves to investigate the constitution of acetic acid. It was known that ammonium oxalate² and ammonium formate yielded cyanogen and prussic acid respectively on dehydration. Fehling had lately shown that ammonium benzoate produced benzonitrile under similar treatment, and Schlieper that there existed a valerionitrile. It was also well known that on boiling these cyanides with potash, salts were produced, of oxalic acid from cyanogen, of formic from hydrocyanic acid, of benzoic from benzonitrile, and of valeric from valerionitrile. If Berzelius was right, and benzoic acid should properly be given the formula $\text{HO}.\text{C}_{12}\text{H}_5.\text{C}_2\text{O}_3$, and valeric acid the formula $\text{HO}.\text{C}_6\text{H}_5.\text{C}_2\text{O}_3$, then ethyl cyanide should yield an acid $\text{HO}.\text{C}_2\text{H}_5.\text{C}_2\text{O}_3$. And experiment³ proved their deduction

¹ *Ann. Chem. Pharm.*, 54.

² *Liebig's Ann.*, 49, p. 91.

³ *Memoirs, Chem. Soc.*, 3, p. 386.

valid. It was this belief that methyl cyanide¹ and acetic acid contained the same radical C_2H_3 that led the next year to their attempt at its isolation by heating this cyanide with potassium. True they only obtained its hydride, $C_2H_3.H$, but here was evidence enough of the correctness of their views. And meanwhile Kolbe² had passed a current from six Bunsen cells successively through solutions of potassium valerianate and acetate, and had in both cases obtained striking confirmation of his copulated formulæ, namely, separation of a light oily liquid with the formula C_3H_9 and a gas C_2H_3 respectively at the positive pole, mixed in both cases with carbonic acid, and free potash at the negative. But in writing acetic acid a copulated oxalic acid, $HO.(C_2H_3).C_2O_3$, Kolbe by no means allowed Berzelius' dogma that the copula C_2H_3 was without influence on the nature of the copulated acid. He probably saw, too, that there was a wide difference between Berzelius' oxalic acid, $C_2O_3(C = 12, O = 16)$, and his own, $(C = 6, O = 8)$, and he was not long in deciding that the fatty acids must be oxides of copulated radicals—substances, that is, having no immediate relationship with oxalic acid at all; so formic acid⁴ he wrote $\widehat{H.C_2O_3}.HO$, and acetic acid $C_2H_3.\widehat{C_2O_3}.HO$.

This was in 1848. The complex C_2 , then, was the determining unit of composition in these substances; H and C_2H_3 were the copulæ, which, while leaving unaffected the combining powers of C_2 , yet did make themselves felt through the properties of the acids in which they occurred. And was there any evidence for this buckle theory of Kolbe, as Gerhardt scornfully called it? Certainly, for did not cacodyl exist, a substance which could only be regarded as arsenic coupled with methyl, $As(C_2H_3)_2$, and which yet retained the power of combining with one or three atoms of oxygen just as arsenic did; was there not sulphur coupled with methyl and ethyl, $(C_2H_3)S_2$ and $(C_4H_5)S_2$, in methyl and ethyl disulphonic acids?

¹ *Ann. Chem. Pharm.*, 4, p. 288.

² *Mem. Chem. Soc.*, 3 (1848).

³ *Quart. Journ. Chem. Soc.*, 2, p. 187.

⁴ Cf. Kolbe, *Zur Entwicklung der Theor. Chem.*, p. 9.

If further confirmation of the tenability of Kolbe's theory was needed, it came most forcibly from the research on zinc methyl,¹ which Frankland prosecuted the following year, 1849. After preparing "free methyl" by heating methyl iodide with zinc, Frankland had found a white residue left in his tube, which on distillation in an atmosphere of hydrogen gave a clear liquid of nauseous odour, which on contact with air inflamed spontaneously with deposition of zinc and zinc oxide on neighbouring cold surfaces, and which, dropped into water, decomposed with extraordinary violence, marsh gas or methyl hydride being eliminated. The liquid could only be a compound of zinc with the methyl radical, for which he proposed the name zinc methyl. He opined, doubtless in mind of Bunsen's cacodyl, that the zinc methyl would play the part of a radical, combining directly with oxygen, chlorine, and iodine. And as this question of the existence of organo-metallic compounds was enticing, Frankland now entered on a more extensive research,² and three years later was ready with a paper that marks a new epoch. From the action of tin on ethyl iodide he obtained straw-coloured needles with the composition $\text{SnC}_4\text{H}_5\text{I}$; from these, by the action of caustic potash, a solid oxide of stannous ethyde $\text{SnC}_4\text{H}_5\text{O}$; and by contact with a strip of zinc, oily yellow drops of the ethyde itself SnC_4H_5 . He obtained very similar results by substituting mercury for tin, and meanwhile Löwig and Schweitzer had succeeded in preparing the three substances stibethine $(\text{C}_4\text{H}_5)_3\text{Sb}$, binoxide of stibethine $(\text{C}_4\text{H}_5)_3\text{SbO}_2$, and oxide of stibmethylium $(\text{C}_2\text{H}_5)_4\text{SbO}$. Now Frankland had begun his investigation in the belief that these organo-metallic compounds were substances containing metal copulated with a hydrocarbon radical, substances which should be capable therefore of combining with oxygen and chlorine in just such measure as would their contained metal. But experiment had proved this belief false. Metallic tin formed two oxides, SnO and SnO_2 , two chlorides, SnCl_2 and SnCl_4 ; metallic antimony had two oxides, SbO_2 and SbO_3 , similarly arsenic. Yet, copulated with

Frankland
discovers
the
organo-
metals.
Valency.

¹ *J. C. S.*, 2, p. 297.

² *Phil. Trans.*, 142, p. 417.

ethyl, tin formed but one oxide, $\text{SnC}_4\text{H}_5\text{O}$, and one chloride, $\text{SnC}_4\text{H}_5\text{Cl}$. The highest oxide of copulated antimony was $(\text{C}_4\text{H}_5)_3\text{SbO}_2$, while the most powerful oxidizing agent was without effect on cacodylic acid $\text{As}(\text{C}_2\text{H}_3)_2\text{O}_3$. And then he thought of his experience in the inorganic laboratory, and all became suddenly clear. In his own words: "When the formulæ of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony, and arsenic especially, exhibit the tendency of these elements to form compounds containing three or five atoms of other elements; and it is in these proportions that their affinities are best satisfied; thus in the ternary group we have NO_3 , NH_3 , NI_3 , NS_3 ; PO_3 , PH_3 , PCl_3 ; SbO_3 , SbH_3 , SbCl_3 ; AsO_3 , AsH_3 , AsCl_3 , etc.; and in the five-atom group, NO_5 , NH_4O , NH_4I , PO_5 , PH_4I , etc. Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident from the examples just given, that such a tendency or law prevails, and that no matter what the character of the uniting atoms may be, the combining power of the attracting element (if I may be allowed the term) is always satisfied by the same number of these atoms."

Kolbe and
acetic acid.

Let us return to Kolbe and his formula for acetic acid, $\text{C}_2\text{H}_3\text{C}_2\text{O}_3\text{HO}$.¹ "If now," said he, "we could succeed in producing by the action of methylic iodide upon ferric carbide FeC_2 a radical of the composition $(\text{C}_2\text{H}_3)\text{C}_2$, which combines directly with oxygen to form acetic acid, no one would hesitate to regard this radical as acetyl, and to place acetyl in the same category with mercurous methide (HgMe) and stanethide (SnEt_2)." Immediately Kolbe, and with him Frankland, was prepared to regard acetic acid $\text{C}_2\text{H}_3\text{C}_2\text{O}_3$ as derived by substitution from carbonic acid C_2O_3 just as cacodylic acid $(\text{C}_2\text{H}_3)_2\text{AsO}_3$ was derived from arsenic acid AsO_5 . It was not, however,

¹ *Ann. Chem. Pharm.*, 101, p. 257 (written in 1856).

till 1858, when Wanklyn,¹ by acting on carbonic acid with sodium ethyl, brought about the direct substitution of oxygen by the ethyl radical with production of sodium propionate ($\text{C}_6\text{H}_7\text{C}_2\text{O}_3$) and they had themselves been equally successful with zinc ethyl, that Kolbe and Frankland felt really secure in their assumption. To Kolbe, then, hydrated acetic acid was a binary compound, in the sense of Berzelius, of water HO and an acid (C_2H_3) C_2O_3 . The two carbon atoms outside the copula were quite different in function from the other carbon atoms, forming together the unit whose affinities held together in one molecule the remaining single atoms or radicals. This unit, the C_2 group—Kolbe called it carbonyl—in organic acids was always found combined with four other units, oxygen atoms or alcoholic radicals. Sometimes one of these oxygen atoms was substituted by a chlorine atom, sometimes by an amido group, whence there resulted acid chlorides or amides, (C_2H_3) $\text{C}_2\text{O}_2\text{Cl}$ and (C_2H_3) $\text{C}_2\text{O}_2\text{NH}_2$, for example.

There has been much discussion from time to time as to whether Kolbe at this period did recognize the tetravalency of carbon. It has been attempted to do great honour to Kekulé, and this with his sanction and active assistance, by claiming for him priority in this regard. It is urged that Kolbe did not expressly state the group C_2 to be tetratomic till after the publication of Kekulé's paper² on the copulated radicals in 1857; that even were the unexpressed tetravalency of his C_2 group the foundation of his whole system subsequent to 1856, it could have no bearing on the tetratomicity ascribed by Kekulé to the single atom of carbon in 1857. Yet it would appear that if one disallows Kolbe's understanding of the tetratomicity of his carbonyl group, one must disallow Frankland's understanding of the divalency of tin, of the pentavalency of arsenic, in which case his words can have no meaning. It is certain that for Kolbe the C_2 in carbonic, acetic, and homologous acids required four units for complete

Kolbe and Kekulé and the tetravalency of carbon.

¹ *Ann. Chem. Pharm.*, 107, p. 125.

² *Ibid.*, 104, p. 129.

saturation, just as arsenic in cacodylic acid required five. Frankland's thesis being accepted, the point was so clear that it was superfluous to lay stress on it. For the rest, Kolbe's C_2 of 1856 and Kekulé's C of 1857 were, as both recognized, different expressions of the same physical entity; but the one was more suitable in the presentment of organic molecules as aggregates of associated chemical units, the other in their presentment as derivatives of the single carbon atom.

Kolbe's
generaliza-
tions.

Kolbe¹ then regarded C_2 as a group with a tendency to combine with four monatomic atoms or radicals; it was at times satisfied with two, and sometimes perhaps with one. So one might regard carbonic acid C_2O_4 as the mother substance of one series of compounds, C_2O_2 of a second, and the hypothetical C_2O of a third. "In fact, organic substances are one and all derivatives of inorganic compounds, and can be prepared from these, in part directly, by wonderfully simple substitutions." So we have the series—

$2HO.[C_2O_2]O_2$ carbonic acid

$HO.H[C_2O_2]O$ formic acid

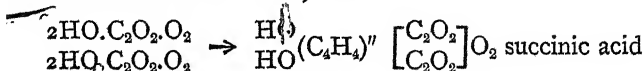
$HO.C_2H_3[C_2O_2]O$ acetic acid

$\begin{matrix} H \\ | \\ C_2H_3 \end{matrix} [C_2O_2]$ aldehyde

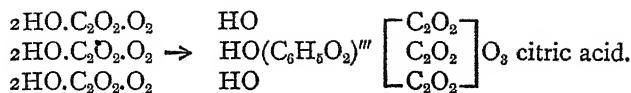
$\begin{matrix} C_2H_3 \\ | \\ C_2H_3 \end{matrix} [C_2O_2]$ acetone

Organic acids, then, contained the radical C_2O_2 , and oxygen atoms outside the radical; the number of these determined basicity, that is the number of equivalents of water with which the anhydrous acids combined.

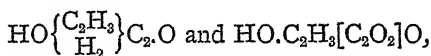
Hofmann, in 1858, had shown that the combination of a diatomic radical with ammonia produced a diamine, a triatomic radical a triamine. Kolbe assimilated the idea, and derived the di- and tri-basic organic acids from two and three molecules of carbonic acid; thus—



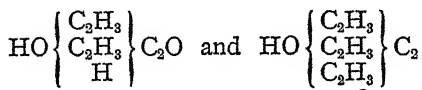
¹ *Liebig's Ann.*, 113, p. 293 (1860).



The relation between alcohol and its oxidation product, acetic acid, he indicated by the formulæ—



from which it would appear that there was every reason to suspect the existence of quite other types of alcohols with formulæ—



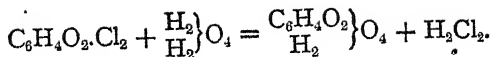
for example, the first of which would readily oxidize to form a ketone, $\left\{ \begin{array}{c} \text{C}_2\text{H}_3 \\ \text{C}_2\text{H}_3 \end{array} \right\} \text{C}_2\text{O}_2$, the second of which, however, would be unaffected by oxidizing agents. Confirmation of these deductions had not to be waited for long, for in 1862 Friedel isolated secondary propyl alcohol, and in 1864 Butlerow tertiary butyl alcohol.

In 1850 Kolbe suggested the formula $\text{HO.C}_{12}\text{H}_4.\text{NH}_2[\text{C}_2\text{O}_3]$ for the so-called benzamic acid, obtained by the reduction of nitrobenzoic acid. In 1854 his pupil, Gerland, by acting on the benzamic acid with nitrous acid, obtained oxybenzoic acid, $\text{HO.C}_{12}\text{H}_4.\text{HO}_2[\text{C}_2\text{O}_3]$ as Kolbe wrote it. Kolbe at once saw the bearing of this result on the fuller knowledge of kindred compounds. Glycocollic must be amidoacetic acid $\text{HO.C}_2\text{H}_2.\text{NH}_2[\text{C}_2\text{O}_3]$, and glycollic acid oxyacetic $\text{HO.C}_2\text{H}_2.\text{HO}_2[\text{C}_2\text{O}_3]$. Again, alanine must be written $\text{HO.C}_4\text{H}_4.\text{NH}_2[\text{C}_2\text{O}_3]$, and lactic acid $\text{HO.C}_4\text{H}_4.\text{OH}_2[\text{C}_2\text{O}_3]$.

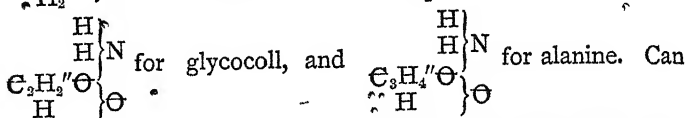
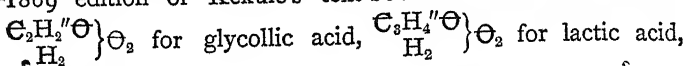
In the year 1858¹ Wurtz, acting on lactic acid with phosphorus pentachloride, obtained a substance which he felt could only be formulated $\text{C}_6\text{H}_4\text{O}_2.\text{Cl}_2$. He treated this body with water, and expressed the ensuing reaction thus—

Constitution action according to Wurtz and Kekulé.

¹ *Liebig's Ann.*, 107, p. 194.



It matters not for our purpose that no lactic acid is in reality formed under such conditions. The equation illustrates Wurtz' philosophy, if not his experimental skill. And in the 1869 edition of Kekulé's text-book we find the formulæ



one greatly wonder at Kolbe's scornful comment, "Such one calls chemical constitution"?

Fortune of
the type
theory.

Kolbe's criticisms of the type theory were extremely harsh; anything which savoured of an attempt to get at the physical constitution of chemical substance seemed to him not merely foolish, but pernicious; nor would he allow that the typical formulæ proposed did in any way advance one's knowledge of the reaction character of such substance. Yet Kolbe stood alone. Since the publication of Gerhardt's treatise, the whole chemical world had given itself up to foster his theory, and much elucidatory and experimental work of the first order had resulted. And very necessary to a confident taking of the next step this was, for Frankland's belief in the definite saturation capacity of each element had not yet become widespread, perhaps, indeed, because its inception was in no wise associated with the prevailing creed.

Odling¹ in England, in 1854, generalizing from Williamson's idea of the double water type, sought to show how every oxide, every oxy-acid or salt, might profitably be referred to a single or multiple water molecule; how it seemed quite reasonable to regard them as one, two, or more molecules of water with some or all the hydrogen atoms replaced by other atoms or groups of atoms. So stannic² acid might be written $\left. \begin{smallmatrix} \text{Sn}'' \\ \text{Sn}'' \end{smallmatrix} \right\} 2\text{O}''$,

¹ J. C. S., 7, p. I.

² Cf. Kopp, *Entwicklung der Chemie*, pp. 776-789.

bismuth oxide $\text{Bi}''' \left. \vphantom{\text{Bi}'''} \right\} 3\text{O}''$, phosphoric acid $(\text{PO})''' \left. \vphantom{(\text{PO})'''} \right\} 3\text{O}''$, and sodium sulphate $(\text{SO}_2)'' \left. \vphantom{(\text{SO}_2)''} \right\} 2\text{O}''$, a very considerable advance on the old empiric formulæ of Berzelius, or the equivalent formulæ of Gmelin and the French school.

In France Berthelot¹ was busy with glycerine. Years before Chevreul had found this substance separated on the saponification of many fats; but it had remained for Berthelot to show that it could combine with one, two, or three molecules of monobasic organic acid, eliminating, as the case might be, one, two, or three molecules of water, just as Graham had found to be the case with phosphoric acid and soda. Wurtz was happy in his reference of glycerine $\text{C}_3\text{H}_5''' \left. \vphantom{\text{C}_3\text{H}_5'''} \right\} \text{O}_3$ to the triple water type $\text{H}_3^3 \left. \vphantom{\text{H}_3^3} \right\} \text{O}_3$, and happier still in his prognostication of an alcohol $\text{C}_2\text{H}_4'' \left. \vphantom{\text{C}_2\text{H}_4''} \right\} \text{O}_2$, referable similarly to the double water type; but happiest was he in the brilliant investigation which followed; for he found that the substance produced by the action of silver acetate on ethylene iodide, when boiled with potash, yielded this very alcohol glycol. But even before this experiment of Wurtz, H. L. Buff had shown that ethylene must be diatomic, since its iodide with potassium sulphocyanide

formed a substance $\text{Cy} \left. \vphantom{\text{Cy}} \right\} \text{S}_2$
 $\text{C}_2\text{H}_4 \left. \vphantom{\text{C}_2\text{H}_4} \right\} \text{S}_2$. So we find spreading through

England and France a belief in the definite saturation capacity of the radicals, and at the same time of the constructive vitality of the type theory.

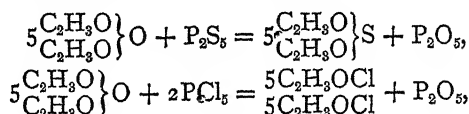
The simpler compounds of inorganic chemistry readily found place in the type system, as did also the more complex of organic chemistry, provided one was content to take homologous radicals for granted. But the analytic faculty had been aroused, and there was seen no reason why carbon compounds alone should be absolved from exhaustive criticism, why the

¹ *Comptes Rendus*, 38, p. 668.

facts of homology should not find explanation in the chemical nature of the organic element carbon, as the constitution of bismuth oxide in the affinities of its metal. It is pre-eminently the merit of Kekulé to have finally solved this question of the chemical nature of carbon. Let us follow the train of his experiments and deductions.

Kekulé introduces the marsh-gas type.

August Kekulé, in 1854, was investigating and comparing the action of the sulphide¹ and chloride of phosphorus on various organic substances, and had found the action of the first to be of a very different character from that of the second, that acetic anhydride, for example, might have its typical oxygen replaced by sulphur without further change, but if by chlorine, then the molecule of the anhydride fell into two halves. These results he expressed thus:—



intimating thereby that one atom of sulphur or oxygen was equivalent in combining power to two of chlorine. Convinced, therefore, by his own experiment of the diatomicity of oxygen and sulphur, and with full knowledge of the strivings of the typical school, he was readily satisfied, by his investigation on mercury fulminate in 1857, that a fourth type, the marsh-gas type, should be added to the three maintained by Wurtz. For mercury fulminate² treated with chlorine gave nitropickrin, which with other evidence pointed to a relationship between the two, well expressed thus:—

$\text{C}_2\text{H.H.H.H}$ marsh gas
 $\text{C}_2\text{Cl.Cl.Cl.H}$ chloroform
 $\text{C}_2\text{NO}_2.\text{Cl.Cl.Cl}$ nitropickrin
 $\text{C}_2\text{NO}_2.\text{C}_2\text{N.Hg.Hg}$ mercury fulminate.

¹ *Ann. Chem. Pharm.*, 90, p. 309.

² *Ibid.*, 101, p. 200.

In the same year Kekulé¹ delivered himself of his opinions on the so-called copulated compounds. It was time, indeed, that this term and the vagueness of idea which it implied were banished from chemical nomenclature. To Berzelius the copula had been merely a kind of forced aggregation of all those atoms in a compound which he could not functionally account for; and though to Kolbe, with his yet undefined sense of definite saturation capacity, the copula still meant something more, it was for him also a confession of failure; while Gerhardt's use of the term was so different that it either meant nothing at all, or was sufficiently covered by the term radical. Kekulé showed that a body, whether of the so-called copulated order or not, was dependent for its integrity on the play of the one force, chemical affinity, acting through the individual atoms. All substances might be referred to a simple type, a plural type, or, as he now showed, a mixed type, and there was nothing mysterious about the fact that these combined similar or dissimilar types offered a scheme for constitution; it was merely a question of there being present some atom or radical which, being polyatomic, could at the same time replace an atom in each of the several typical substances, and so hold them together. Thus sulphuric

acid SO_2 } \ominus might be referred to the hydrogen-water type

$\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{matrix} \left. \vphantom{\begin{matrix} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{matrix}} \right\} \ominus$, so, too, methyl sulphite $\begin{matrix} \text{CH}_3 \\ \text{SO}_2 \\ \text{H} \end{matrix} \left. \vphantom{\begin{matrix} \text{CH}_3 \\ \text{SO}_2 \\ \text{H} \end{matrix}} \right\} \ominus$; carbamic acid $\begin{matrix} \text{H} \\ \text{H} \\ \text{CO} \\ \text{H} \end{matrix} \left. \vphantom{\begin{matrix} \text{H} \\ \text{H} \\ \text{CO} \\ \text{H} \end{matrix}} \right\} \text{N} \left. \vphantom{\begin{matrix} \text{H} \\ \text{H} \\ \text{CO} \\ \text{H} \end{matrix}} \right\} \ominus$

was of the ammonia-water type.

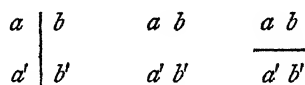
There was nothing very original in all this, as Kekulé allowed; it was merely a clear and comprehensive expression of the teaching of Williamson, Gerhardt, Odling, Wurtz and Buff. But Kekulé's ideas were rapidly clearing; his labours at Giessen, in Paris, and in the proximity of Williamson and Odling in London, enfranchized him from any particular

Kekulé attacks the copula.

Kekulé's philosophy.

¹ *Ann. Chem. Pharm.*, 104, p. 129.

school, and left him in a position to pick what was vital from each, and see all as part of one comprehensive and consistent philosophy. He could now avail himself of the labours of Kolbe, and, where the latter was restrained by the copula, advance in the knowledge of a necessarily polyatomic atom. He knew to the full the value and the limitations of Gerhardt's types; he could add to them the marsh-gas type and turn it to account, still understanding that they meant nothing unless read as a commentary on the chemical nature of the atoms they contained. He had employed up to now the equivalent system of Gmelin; he could readily shake off the shackles which bound Kolbe so hard, and write C , O , S more confidently than Gerhardt. The prevalence of double decomposition as a mode of chemical reaction was as patent to him as to the author of the theory of residues; but double decomposition would not explain the combination of ammonia with hydrochloric acid, of chlorine with phosphorus chloride, of water with succinamide. No, it was only in the knowledge of the combining capacity of the atoms themselves that salvation lay, and in an understanding that the chemical reaction is better expressed thus:—



with allowance for the formation of intermediate products, than in ancient wise—

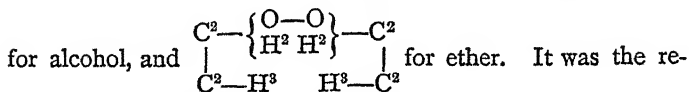
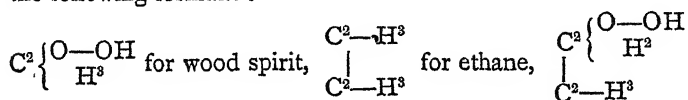
$$ab + a'b' = a'b + a' b;$$

So when in 1858 Kekulé boldly stated carbon¹ to be tetra-atomic, and to be possessed of the power of combining with itself, with loss to each atom of one of these units of atomicity, he was prepared as no man before to face the difficulties of organic constitution. Homology ceased at once to be a problem; saturated hydrocarbons must have the composition

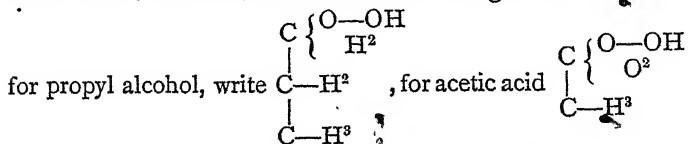
¹ *Liebig's Ann.*, 106, p. 129.

C_nH_{2n+2} ; monatomic hydrocarbon radicals, owing their one unit of atomicity to carbon, must have the formula C_nH_{2n+1} .

In the same year, and quite independently of Kekulé, Couper and the nature of the carbon atom. M. S. Couper published a paper¹ in the *Annales de Chimie et de Physique* almost identical in character and conclusions with that of Kekulé. Couper, too, saw that Gerhardt's theory of types gave no explanation of the facts of combination; that such typical substances as nH_2O had no real existence; that it was mere cowardice to stop short at the radical in pious content with ignorance; that one should rather go to the elements themselves in picturing their intermolecular play, and consider, too, not merely their elective affinities, but their affinities of degree. And especially in the case of the carbon compounds must one understand that each carbon atom has an affinity four times greater in degree than that of hydrogen, chlorine, or oxygen, and that carbon atoms can combine with other atoms of the same element. One would be so led to the following formulæ:—



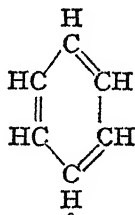
lation between ether and alcohol which prevented Couper's accepting the $O-O$ of his formula as really signifying but one atom of oxygen, though his atoms, O , were never found separate. On the other hand, the constant occurrence of C_2 rather than C made him double the atomic weight of carbon, and,



Thus with the publication of Kolbe's, of Kekulé's, and The formula of benzene.

¹ *Ann. Chim. Phys.*, 53, p. 469.

Couper's papers the enigma of organic constitution was solved for all who would take the pains, solved, that is, within the limits of purely chemical investigation. There now only remained the clerical labour of accumulating details to build up the organic text-book of to-day; for even Kekulé's speculation on the constitution of the aromatic substances was but an adaptation of his new philosophy to a particular case, and was brilliant rather in its material results than its inception. Yet eight years had to elapse before Kekulé advanced from the chemical nature of carbon to the ring formulæ of the aromatic compounds. He had to meet the following facts.¹ All aromatic substances, even the simplest, are proportionally richer in carbon than analogous fatty compounds, and never contain less than six such atoms in the molecule; moreover, whatever be the chemical change they undergo, unless this be in the nature of a complete disruption of their molecules, decomposition ceases with the reduction of the carbon content to six atoms. Finally, homology obtains among aromatic compounds just as commonly as among fatty. In suggesting the formula—



for the mother substance benzene, Kekulé felt that he was well within the speculative boundaries imposed by the chemical nature of carbon heretofore ascertained, that he was distinctly marking the generic difference between aromatic and empirically analogous fatty or chain compounds, and that in exemplifying the number and nature of cases of isomerism which must necessarily ensue according to the number and

¹ *Ann. Chem. Pharm.* (1866), 137, p. 129.

position of the hydrogen atoms substituted, he was offering to time and experience an infallible test by which his theory must stand or fall. Twenty-five years later, in 1890, there was held a magnificent festival in honour of this most masterly product of deductive reasoning. There had been found no flaw, and chemists in their syntheses had gone on from strength to strength with the benzene ring fixed on their mental horizon as firmly as the planetary system of Copernicus. Since the day when Kekulé exposed the chemical nature of carbon there has occurred nothing which has led, or could lead, organic chemistry into a new phase. The organic text-book of to-day is the history which the student must consult who would learn of the progress in methods of synthesis and diagnosis; it is all found in embryo in Kekulé's tetravalent carbon atom with the power of combining with itself.

Long seems the road with many a by-way from Kolbe's substituted carbonic acids to the multitudinous, complex, and acutely reasoned formulæ of to-day; and it is long but straight, and few are the landmarks and not many the accidents Kolbe did not point out and foresee in his wonderful philosophy. To the unaccustomed eye, Kolbe's formulæ seem so strange with their equivalent notation that the soundness of his attitude is not at once apparent. It was not till 1870 that he consented to write $O = 16$, $C = 12$, $S = 32$. His formulæ for alcohol, $HO\left\{\begin{smallmatrix} C_2H_3 \\ H_2 \end{smallmatrix}\right\}C_2O$, and for acetic acid, $HO.C_2H_3$

The validity of Kolbe's formulæ.

$[C_2O_2]O$, by a natural transition, then became $\begin{smallmatrix} CH_3 \\ H_2 \end{smallmatrix}C.OH$ and CH_3CO

$\begin{smallmatrix} O \\ H \end{smallmatrix}$, and a little thought will convince that, granted the dualism of organic substance and the integrity of the two portions, Kolbe's expressions were as correct before as after this transition.

Yet we have not completely traced the history of our modern conception of the organic molecule; something great has been done since the time of Kekulé, but this has been

outside, not inside, the molecule. The relative size and the spacial construction of the molecule were questions which, as Kekulé long ago maintained, must be left for the physicists to settle, and these have since worked worthily. To the history of the molecule as a physical structure we must now turn.

CHAPTER XII

THE DEVELOPMENT OF STEREO-CHEMISTRY

So long ago as the year 1669 Erasmus Bartholinus had noticed that an object, when viewed through a plate of Iceland spar, appeared double. Bartholinus had further discovered that while the rays producing one image obeyed the ordinary laws of refraction, the others did not. But it was only after the lapse of more than a century, and after Huygens¹ and Newton had taxed themselves in vain with the explanation of this case of double refraction, that knowledge came. In 1810 Malus, glancing through a doubly refracting prism of quartz at the light reflected from the windows of the Luxembourg Palace, noticed that this light had acquired those same qualities which came from passage through Iceland spar. Imbued as he was with a belief in Newton's corpuscular theory, and with the sense of an analogy between the duplicity of light rays and magnetic two-endedness, he termed the phenomenon polarization. The corpuscular theory being powerless to explain this polarization, and so, too, the undulatory theory as then conceived, attention was drawn to an old guess of Hooke, that to produce a sense of light the vibration of the ether must be in a plane perpendicular to that of progression; and soon, through the efforts of Young, Fresnel, and others, there arrived conviction that while ordinary light resulted from the vibration occurring simultaneously in all directions in this perpendicular plane, polarized light acquired its peculiar properties from the ether vibrating in but one direction.

The discovery of the polarization of light.

¹ Cf. P. G. Tait's article, *Ency. Brit.*, 14, p. 611.

Association of polarization and the hemihedral form.

Now, Biot, after discovering that polarized light b^y passing through a quartz plate had its direction of vibration rotated through an angle depending on the thickness of the plate, proceeded to show that turpentine, and other organic bodies, sugar, camphor, and tartaric acid—these in solution—exerted a similar effect on polarized light. In these latter cases this rotary power must certainly come from the activity of the smallest dissolved particles, the molecules, and not, as in the case of quartz, from the nature of the crystalline form. Biot had found, too, that of his various quartz plates some rotated the plane of polarization to the left, others equally to the right. The great crystallographer Hauy¹ had discovered quartz to be among those minerals which exhibit hemihedrism; moreover, that there were two hemihedral forms of quartz identical in every respect but this—they were not superposable, the one appearing as the reflected image of the other. In 1820 Sir John Herschell demonstrated to the Royal Society that in this discovery of Hauy lay the explanation of Biot's converse results; that it was the right-handed hemihedron of quartz which turned the plane of polarization to the right, the left-handed which turned it to the left.

The optical activity of certain organic substances. Pasteur's work.

It is a curious fact that no one thought of connecting the then well-known activity of sundry organic substances with a possible analogy in their crystalline forms. Not till nearly thirty years had elapsed did a mind waken to the intimate relationship which must hold between rotation of light and physical, perhaps chemical, structure. Then Pasteur began to investigate the tartaric and racemic acids. In the massed crystals of all the tartrates he found traces of hemihedral forms, all in the same sense. Racemic acid, inactive to light, gave no hemihedra. Mitscherlich, in 1844, had given to the Berlin Academy an account of an extended research into the physical character of the sodium ammonium tartrate and racemate; he had found these salts identical in all respects save one: the tartrates were active on polarized light, the racemates not. Pasteur could make nothing of this, so he

¹ Pasteur, *Ostwald's Klassiker*, 28, p. 8.

repeated Mitscherlich's experiments, and with results that amazed him. True enough the tartrates crystallized in hemihedra; but the racemates, they crystallized in hemihedra too! While, however, the hemihedra of the tartrates were all in one sense, those of the racemates were mixed equally in opposite senses. These, carefully separated and dissolved, gave solutions rotating polarized light to the right and left, yielded acids of similar optical character, which, mixed in equal quantities, combined with evolution of heat to form racemic acid. Pasteur repeated his experiments before Biot. "My dear child," exclaimed the veteran, "I have my life long so loved the science, I hear my heart throb with joy." And it was not long before Pasteur found other means of separating the component parts of racemic acid. He neutralized the acid with the active base cinchonine, and found that on crystallization the lævo cinchonine tartrate separated first, later the dextro salt in a quite different form. Moreover, under the influence of yeast, ammonium racemate rapidly became lævorotatory, all the dextrotartrate it contained being destroyed. So the explanation of the isomerism of the tartrates lay in this: the molecules were similarly constituted of the same atoms, but these atoms were arranged in the two in just the reverse order. There was a pleasant elation about Pasteur's closing words, "I have, in fact, set up a theory of molecular asymmetry. I have opened one of the weightiest, most astonishing chapters in science—one which offers to physiology a horizon, new, far-distant, yet quite distinct."

In the 1867 edition of his great text-book ¹ Kekulé drew attention to a number of cases of isomerism which at that time had received no explanation. Among these we find that of ethylene chloride with ethylidene chloride; of acetal with diethyl glycol; for maleic and fumaric, for mucic and saccharic acids, the last effort of his philosophy had only found him the two formulæ $\begin{matrix} \text{C}_4\text{H}_2''\text{O}_2 \\ \text{H}_2 \end{matrix} \} \Theta_2$ and $\begin{matrix} \text{C}_6\text{H}_5''\text{O}_2 \\ \text{H}_2 \end{matrix} \} \Theta_2$ respectively, Kekulé

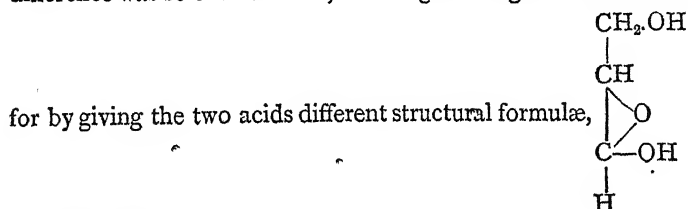
Kekulé
and
isomerism.

¹ Cf. 2, p. 189.

instanced too those bodies which only differed in their effect on polarized light, the tartaric, the malic and camphoric acids, and the amyl alcohols. He had been careful to insist that none of his formulæ were other than mere reaction formulæ, yet had by no means escaped the ire of his countryman Kolbe. Kolbe seemed to see the cloven hoof in every page of the book; and one can well understand the bitter scorn, if one cannot pardon the gross personalities, with which he greeted the publication of Van t' Hoff's *La chimie dans l'espace*, which, in its Germanized form, appeared in 1877. Had not the work been foisted (in Kolbe's opinion) on the public under the protecting ægis of Kekulé's and Wislicenus' patronage, he had not condescended to notice it.

Wislicenus
and the
lactic
acids.

✓ Wislicenus¹ had indeed some cause to hail with delight so clear a formulation of views which, years before, he had seen could alone reconcile facts with established theory. He had been occupied with the various modifications of lactic acid. He had found that the ethylene lactic acid or hydracrylic acid prepared by Beilstein, by treating β -iodo-propionic acid with silver oxide, possessed properties different from those of the ethylene lactic acid obtained from ethylene cyanhydrin. The difference was so considerable, he thought it might be accounted

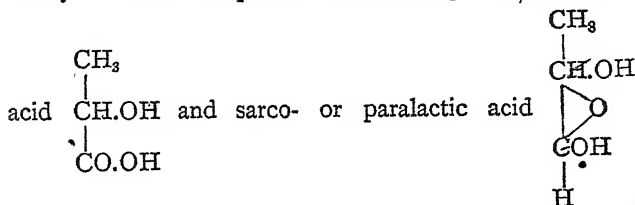


and $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2 \\ | \\ \text{COOH} \end{array}$ respectively. The fermentation lactic acid and the sarcolactic acid of Liebig,² both ethylidene lactic acids, were in chemical properties identical, yet they differed in that

¹ *Liebig's Ann.*, 166, p. 3.

² *Ibid.*, 167, p. 302.

the first was inactive towards polarized light, while the second was dextro-rotary. This one point of difference seemed hardly sufficient to permit one's writing fermentation lactic



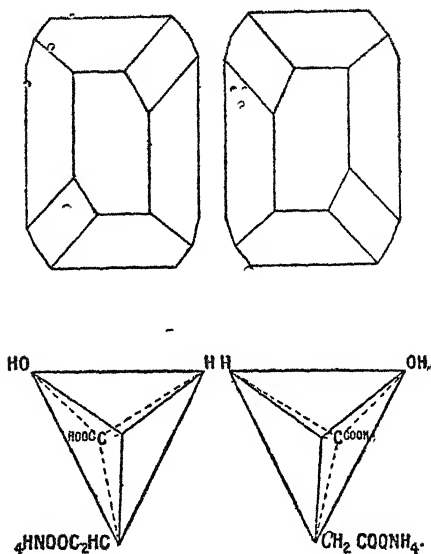
seemed much more likely that here, at any rate, were cases of what Carius had called physical, but what Wislicenus now proposed to call geometrical isomerism. "I must recognize," he says, "these differences in property as the result of a different *spacial ordering* of the atoms in the molecule."

Van t' Hoff's brochure,¹ *La chimie dans l'espace*, contained a synopsis of two papers, published almost simultaneously and quite independently in 1874, the one by the French chemist, Le Bel,² the other by the author. The theses of both were the same—Pasteur having established the correlation of molecular disymmetry and rotary power, it only remained to discover under what conditions the disymmetry could obtain in two molecules structurally identical. It could not be that the atoms or radicals satisfying the four valencies of carbon were in one plane, for otherwise there would be possibility, nay probability, of isomerism among the mono- and di-substituted methanes. On the other hand, were the four valencies of carbon active towards the angles of a regular tetrahedron, with these valencies satisfied by four different radicals, there would be a possibility of just such a case of isomerism as Pasteur had foreseen. If this was indeed the case, and if the converse rotation of structurally identical bodies found thus its explanation, one would expect, thought Le Bel, to find a carbon atom so bound associated always with optical activity, and, added Van

The theses
of Le Bel
and Van
t' Hoff.

Cf. J. E. Marsh's translation (Oxford).
Bull. Chem. Soc., Paris, November part.

Van t' Hoff, we find indeed that "every carbon compound which in solution rotates the plane of polarized light, does contain such an asymmetric carbon atom." Below we have diagrams depicting and interpreting the hemihedral forms of ammonium bimalate; a glance at them will make clear the relation between Pasteur's evidence, his deductions, and their realization by Le Bel and Van t' Hoff:—

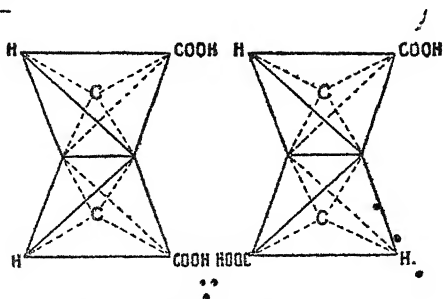


It will be readily observed that the crystals and the two tetrahedra only differ respectively from each other in this, that the one appears as the non-superposable image of the other.

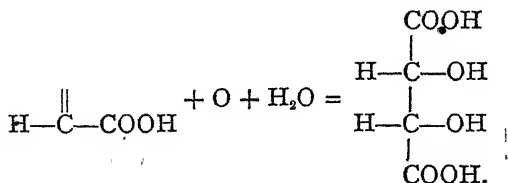
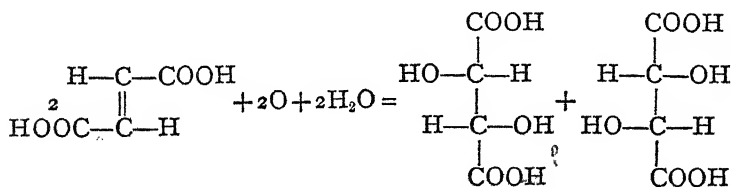
The isomerism of maleic and fumaric acid.

Not only was the different optical activity of certain saturated bodies of identical chemical structure explained by this new hypothesis, but, also the more marked reaction differences of the isomeric fumaric and maleic acids, the citra-, ita-, and mesaconic acids. According to Van t' Hoff, maleic

and fumaric acids would find adequate spatial presentation by the forms—

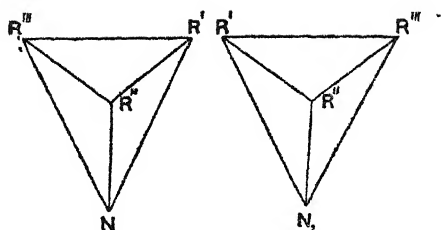


We know how readily maleic acid loses water with production of its anhydride; how, too, fumaric acid, under the influence of temperature, loses water with formation of the very same anhydride. Kekulé and Anschütz, in 1880, found, moreover, that fumaric acid yielded racemic, maleic inactive tartaric acid, on oxidation with permanganate of potash. The new stereochemical philosophy makes the reaction almost obvious—

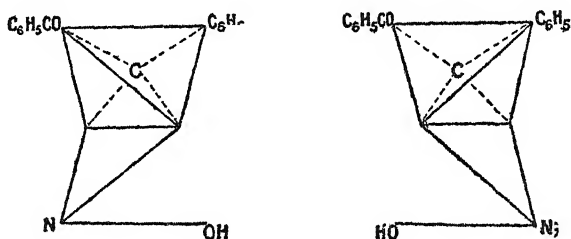


Wislicenus¹ has shown how well in keeping with this picturing is the ready production of fumaric acid from maleic through the intervention of hydrochloric acid. By addition of

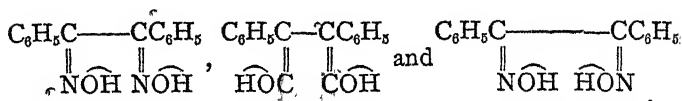
¹ *Berichte*, 12, p. 2282.



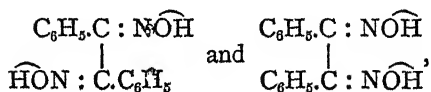
an activity not yet observed, but it offers a reasonable explanation of the existence of certain isomeric oximes and hydrazones of undoubtedly identical structure. There are two benzil monoximes differing markedly in the ease with which they give up water. Hantzsch and Werner see in this evidence of the physical structure—



the corresponding dioximes may be similarly differentiated—



though Auwers and Meyer¹ would rather accept the present ment—



¹ *Berichte*, 21, p. 784.

allowing that even singly-linked carbon atoms may in certain circumstances have their free rotation checked.

But it is not only in the world of the organic chemist that enigmatical cases of isomerism are found. There are many compounds of cobalt, of platinum, ruthenium, and other metals which bind ammonia in measures that seem impossible *a priori*, which have brought Werner to the rescue with a view of interspatial relation between component atoms that is given full honour in so reputable a text-book as that of Roscoe and Schorlemmer.¹

Stereo-chemistry of inorganic compounds.

And so the beginnings of a real structural chemistry are ours. We feel that such a fulfilment awaits it as has already arrived to Dalton's atomic prognostications in the modern constitutional formula. To us, convinced that the physical structure of the molecule is really within mental ken, it matters just as little that for the present we must be content to try this and that presentment, as it mattered to convinced atomists in the times of Dalton that this or that atomic weight was arbitrarily taken as at least a workable unit.

The philosophical world is very conservative, and the man must needs be bold who would attempt to shake it from a long-cherished fallacy. Le Bel and Van t' Hoff had ventured much in propounding a scheme of stereo-chemistry, and they are among those fortunate enough to have seen their courage rewarded. The wonderful fruitfulness of their conception has done much to weaken the hold of revered authority, and we are scarcely surprised to find even so anarchic a suggestion as fluidity of chemical structure received with mere interest. Yet if there was one belief which seemed more firmly founded than another it was this, that substituting radical and radical substituted exchanged function and place. Gerhardt and Kekulé had talked much about mere reaction formulæ, piously allowing the limitations of the human mind; yet they had never seriously supposed that one substance could at one

Tauto-merism.

time have two formulæ suggestive of functions absolutely irreconcilable. Van t' Hoff had been moved to his achievement by the inability of existing theory to meet facts; with Zincke's discovery of the identity of α -naphthoquino-phenyl-hydrazone and phenylazo- α -naphthol, of $C_6H_5HN_2=C_{10}H_6=O$ with $C_6H_5N=N=C_{10}H_6\bar{O}H$, Conrad Laar,¹ in 1884, was in turn made a revolutionary. He recalled other instances where chemical property seemed to demand different formulæ for the same substance,—of prussic acid, whose derivatives suggested the

expressions $N\equiv CH$ and $C\equiv NH$, of cyanic acid, $\begin{array}{c} N \\ \parallel \\ C \\ \diagup \\ OH \end{array}$ and $\begin{array}{c} NH \\ \parallel \\ C \\ \diagdown \\ O \end{array}$, of aceto-acetic ether, $CH_3.CO.CH_2.COOEt$ and

$CH_3COH=CH.COOEt$; and finally of the well-known nitrous acid, $HO.NO$ and $H.NO_2$. Examine prussic, cyanic, nitrous acid, or aceto-acetic ether, and one finds no symptom of their being heterogeneous; examine their derivatives, and one finds them with properties demanding the formulæ $N\equiv CM$ and

$C\equiv NM$, $\begin{array}{c} N \\ \parallel \\ C \\ \diagup \\ OM \end{array}$ and $\begin{array}{c} NM \\ \parallel \\ C \\ \diagdown \\ O \end{array}$, $MO.NO$ and $M.NO_2$, abso-

lutely finally fixed. Here are new phenomena, for which the term "tautomerism" is as serviceable as any; here are substances whose salient hydrogen atoms seem to have no settled position, to be combined one instant with one element, and the next with another. And more recent investigation has only confirmed us in Laar's belief that a modification of our views on molécular stability is necessary. The truant hydrogen atoms have been tracked to their various homes and fixed there. For Claisen² has shown how the substance prepared by Emil Fischer from sodium benzoyl acetone by mixture with benzoyl

¹ *Berichte*, 17, p. 3030; 19, p. 730.

² *Liebigs Ann.*, 291, p. 25; cf. Wislicenus, *Sammlung Chemischer and Chemisch-technischer Vorträge*, 2, p. 187.

chloride exists in two forms entirely different in atomic structure

and physical property, the one, the α form $\begin{array}{c} \diagup \text{COH.CH}_3 \\ \text{C} - \text{CO.C}_6\text{H}_5 \\ \diagdown \text{CO.C}_6\text{H}_5 \end{array}$

melting at 80° , and changing into the β form $\begin{array}{c} \text{CO.CH}_3 \\ \text{HC} - \text{CO.C}_6\text{H}_5 \\ \diagdown \text{CO.C}_6\text{H}_5 \end{array}$

with a melting-point 107° , crystals of which are also obtained after dissolving the α body in alcohol. After shaking the β substance with alcoholic soda, a salt of the original α body remains. There can be no doubt about the virtual existence here of a labile hydrogen atom. Polymerism cannot explain the facts, for the α and β modifications have both the same molecular weight; nor can a possible stereo-isomerism, for the formulæ

$\begin{array}{c} \text{C}_6\text{H}_5 - \text{COH} \\ || \\ \text{C}_6\text{H}_5\text{CO} - \text{C} - \text{CO.CH}_3 \end{array}$ and $\begin{array}{c} \text{C}_6\text{H}_5 - \text{COH} \\ || \\ \text{CH}_3\text{CO} - \text{C} - \text{CO.C}_6\text{H}_5 \end{array}$ are quite

incompatible with the solubility of the one and not of the other in aqueous soda, with the ready action of ferric chloride on the former, and not on the latter.

Why this hydrogen is labile remains a question. Meanwhile Laar has decided to rename the new phenomenon "pseudomerism." Claisen feels that the term "tropomerism," and Jacobson "desmotropy," are to be preferred as lending clearer definition to their views. Finally, it would seem as though the hydrogen atom is not alone to possess freedom of intramolecular movement; the radical ethyl has quite recently been discovered by Claisen to follow sluggishly the lead of its prime homologue. Under the influence of high and sustained

temperature the body $\begin{array}{c} \text{CH}_2 \\ || \\ \text{C}_6\text{H}_5\text{COC}_2\text{H}_5 \end{array}$ becomes $\begin{array}{c} \text{CH}_2.\text{C}_2\text{H}_5 \\ | \\ \text{C}_6\text{H}_5\text{C} = \text{O} \end{array}$

CHAPTER XIII

INTER-RELATIONSHIP OF ATOMIC WEIGHTS, CANNIZ- ZARO'S REFORM, AND THE PERIODIC LAW

EARLIER in this volume I endeavored to trace the development of the atomic theory of Dalton. The broad effect is of Berzelius working, always working, with head and hand to give the atom an assured position. A worthy recompense it would have been to him to know that as he left his theory in 1848, so we find it in 1906—his atoms our atoms, his atomic weights our atomic weights. Berzelius' theory, I say, for he almost alone remained faithful during those first fifty years of its life; and it was with the uninspiring echo of equivalent, mixing weight, proportional number in our ears that we turned to the chemical history of carbon. How came it, then, that the great master being dead, and those left to bear his banner careful merely of analytical nicety, that there gradually came final conviction that the atomic weight was a discoverable and indeed discovered quantity? The answer is instructive as well as interesting, bound up as it is with the answer to that other question: what of the relation of elements to each other?

Döbereiner's
triads.

In 1815 Prout had published his generalization. Human nature being weak, and human intellect greedy of unity, there were plenty to support him. Berzelius was strong enough to remain unmoved; he only pointed to experimental data. It was not to be expected, however, that Prout should wear his laurels alone. Given a sufficiency of numbers, man will play with them if he has nothing better to do. Moreover, he has a rooted disbelief in coincidence. So we are not surprised to.

find a German chemist, Johann Döbereiner,¹ Professor at Jena, only two years after Prout, and probably quite independently of him, calling attention in his lectures to the chemical analogies which mark the elements of the alkaline earths, and to the curious numerical relation shown by their atomic values. Accepting the number 647.285 as the value of strontium oxide, there was but little difference between this and that calculated thus—

$$\frac{356.019(= \text{CaO}) + 956.880(= \text{BaO})}{2} = 656.449(= \text{SrO}).$$

In 1829 Döbereiner published an account of the development of this idea of numerical relationship between the atoms of chemically allied elements. It was with great pleasure he hailed Berzelius' value 78.383 for Balard's new element bromine; for was not this very near the 80.47 already suggested to him, being the mean of the atomic weights of chlorine and iodine, and prophesied by him in his lectures? But there were groups, and many of them, other than those of the halogens and alkaline earths; there were groups whose members were bound by so close a chemical relationship that they, if any, should exhibit some analogous gradation in their atomic weights. Nor was Döbereiner deceived. Here are some of his triads—

$$(\text{O} = 100) \quad \frac{195.310(= \text{Li}) + 589.916(= \text{K})}{2} = 392.613(= \text{Na})$$

[Berzelius' value was 390.897.]

$$(\text{H} = 1) \quad \frac{32.239(= \text{S}) + 129.243(= \text{Te})}{2} = 80.741(= \text{Se}).$$

[The experimental value was 79.263.]

Moreover, if this grouping of the elements by triads was, as seemed not unlikely, to be taken as according with truth, one was led to suspect the existence of elements hitherto undiscovered. For where were the elements which could play third

¹ *Pogg. Ann.* (1829), 15, p. 301; *Ostwald's Klassiker*, 66, pp. 1-8.

to boron and silicon, to aluminium and bismuth, to yttrium and cerium? But Berzelius deemed the triad division of the elements unworthy of remark in his *Jahresbericht*, and it was not till an extended notice appeared in the 1843 edition of Gmelin's text-book that Dobereiner's work met with any general recognition; and, just as with Prout's hypothesis, whose truth could only be vindicated by denial of atomic values hitherto accepted, so too it was with Döbereiner's new system.

Thomson had fared but poorly in his defence of Prout; his table of atomic weights, all nicely rounded off, was very different from that of Berzelius, straight from the laboratory, and rough. In 1829 another Englishman, Turner, took on himself a critical examination of the numbers of Thomson, found the work on which they were based vitiated by one error and another—found, in fact, Berzelius right and Thomson wrong. It is worth notice that Turner about this time introduced the custom of reducing all weighings to vacuum standard, of straining gnats and swallowing camels, as Berzelius grumblingly remarked.

Dumas
disputes
Berzelius'
values for
carbon and
hydrogen.

But as years passed there came evidence—this time very cogent—that some modification was necessary in the equivalent values assigned by Berzelius to the elements. Dumas had analyzed naphthalene again and again with most unsatisfactory results—

C	...	94'3	94'2	94'27	94'9	94'9
H	...	6'3	6'3	6'26	6'2	6'1
		<u>100'5</u>	<u>100'5</u>	<u>100'53</u>	<u>101'1</u>	<u>101'0.</u>

It was clear that either the whole system of organic analysis was wrong, or, as Dumas suggested, the atomic weights for hydrogen and oxygen so patiently accepted under the warrant of Berzelius. To the latter it seemed most likely that the discrepancies were due to experimental error. Berzelius and Dulong, by determining the specific gravities of carbonic acid and oxygen, had obtained, in 1819, the value 12'23 for carbon, a trusted value, which accorded fairly with the 12'14 derived

less surely by heating lead carbonate. For hydrogen Berzelius had given the value 0.998 ($O = 16$), based on determinations of its specific gravity, and on some not very convincing measurements of the water produced by the action of hydrogen on copper oxide. Dumas saw no reason to accept the imputation of experimental inaccuracy thrown out by Berzelius, and with Stas, in 1839, entered on an extensive investigation of the real atomic weight of the all-important element carbon, an account of which appeared in the *Annales¹ de Chimie et de Physique* the following year, sufficiently striking to shake for long all faith in Berzelius' accuracy. Indeed, it was a great paper—a paper which marks an epoch in the history of experimental nicety. Its contents deserve more than a casual glance—

No. of experiments	Carbon used	Weights employed in grms.	Carbon combined with 200 grms of oxygen	Mean
5	Natural graphite from Ceylon	1 : 1.471	75.125 : 74.875	74.96
4	Artificial graphite	.992 : 1.660	74.875 : 75.125	75.01
5	Diamond	.708 : 1.375	74.925 : 75.100	75.02
Mean ...				75.00.

From these they derived as the atomic weight of carbon the number 12 exactly ($O = 16$). At this time Berzelius' value for hydrogen was found to be sufficiently accurate; but three years later Dumas² returned to the labour of estimating this constant beyond cavil. Berzelius' estimations of the water produced in his syntheses had been so discordant that there was no security for the accuracy of their mean. In Dumas' mind, the 10 to 12 grms. collected had been too little, the hydrogen not dry, the neglect shown in not reducing the weighings to vacuum standard inexcusable. With all precaution Dumas made nineteen experiments, the oxygen combined

¹ *Ann. Chim. Phys.* [3], 1, p. 1.

² *Ibid.*, 8, p. 189.

varying from 13.179 to 76.634. The hydrogen found united with 50 grms. of oxygen varied between 6.2360 and 6.2810, with the mean 6.2575, from which he calculated the atomic weight 1.

Dumas
turns to
the law
of Prout.
Petten-
kofer's
views.

Here, then, were two atomic values, measured with the last degree of accuracy, found whole numbers. The significance of this fact did not escape Dumas. "So far," he adds, "the views of Prout have not had that sincere attention which their high importance merits." And now there began keen inquiry into the possible validity of Prout's law. In 1845 Pelouze¹ brought to mind Gay Lussac's method of silver assay, and instigated Marignac to analyze many chlorides and bromides. The atomic weights thus derived mostly agreed well with Prout's hypothesis, and so too those obtained by Erdmann and Marchand. Marignac saw in chlorine alone a real exception, and not even here if the unit were taken as 0.5 instead of 1. There was, however, a difficulty patent to all in accepting a unit so small as 0.5. There were doubts even as to the possibility of deciding the claims of Prout's hypothesis experimentally with the unit even twice that size. As Pettenkofer² pointed out in 1850, were it found that the atomic weights of elements differed by such a number as eight or some multiple of eight, the belief in the complexity of the element, intensified as it was by the discovery of homology, might be turned into something near certainty. Döbereiner's triads suggested that this was indeed the case, but not convincingly; for if there was anything more than mere coincidence in chlorine, bromine, and iodine forming a triad, one would expect fluorine, chlorine, and bromine to form a second triad; similarly magnesium, calcium, and strontium. Yet that there was a relation between groups of elements, closely paralleled by that between the members of a hydrocarbon family, Pettenkofer showed by the following table:—

Cf. Sebelien, *Atomgewichte*, p. 45.

Liebig's *Ann.*, 105, p. 187; Ostwald's *Klassiker*, 66, p. 9, *et seq.*

	Lithium	Sodium	Potassium	
Equivalent weights	$6\cdot51 + 16\cdot46 = 22\cdot97$	$+ 16\cdot14 = 39\cdot11$		
	Magnesium	Calcium	Strontium	Barium
	$12\cdot07 + 7\cdot93 = 20\cdot00$	$+ 23\cdot92 = 43\cdot92$	$+ 24\cdot62 = 68\cdot54$	
	Oxygen	Sulphur	Selenium	Tellurium
	$8 + 8 = 16$	$+ 23\cdot62 = 39\cdot62$	$+ 24\cdot52 = 64\cdot14$	

The differences in the equivalent values of the elements belonging to the same group were all so nearly equal to eight or multiples of eight, that here was surely something more than coincidence. The differences between the equivalents of the elements in the carbon-boron-silicon group and in that of the halogens were similarly found to be some multiple of five. Finally, Pettenkofer maintained that, in view of these facts, in view of the analogy they suggest between the relations of elementary atoms and organic molecules, and our knowledge of such compound radicals as ammonium and cyanogen, "we have lost any scientific guarantee for the undecomposibility of our two and sixty chemical elements." It was some such thesis as this, too, that Dumas was upholding the year following, in 1851, before the British Association assembled at Ipswich. A supposed new element¹ discovered in the thorium mineral, orangite, had suggested to Faraday the possible transmutability of the metals is general, which gave Dumas opportunity for reference to certain triads, to a possible substitution in the so-called elementary atoms analogous to that he knew so well in the organic molecule, and to a remembrance of Prout's hypothesis and his own so recent work on carbon and hydrogen.

This question of a possibly ascertainable relationship between the equivalent weights of the different elements was getting hold of men's minds. In 1853 we find another chemist, this time an Englishman—Gladstone—arranging all the elements in the order of their equivalent numbers, and noticing how great were the gaps between some contiguous numbers, how nearly identical others; how some were multiples of a

Widely
diffused
interest in
the rela-
tionship
of atomic
weights.

Cf. Lothar Meyer, *Ostwald's Klassiker*, 66, p. 28.

constant number, others increased by a definite unit. Gladstone gave full weight to Dumas' Ipswich declamation, as did the American Cooke, for the new phase was felt on the Western Continent too. Cooke¹ even ascribed the discovery of triads to Dumas. Like Gladstone, he was quite unaware of Pettenkofer's work, and, again like Gladstone, was at pains to show how one particular family of elements had equivalent values differing by some multiple of a certain unit. For him there were six such families, and the units marking the differences of their members were 9, 8, 6, 5, 4, and 3 respectively. Papers published by Odling in England, and Lenssen in Germany, were devoted similarly to the search for some new system. They had nothing to say that was very new. Odling had found that of the elements one half had an atomic heat of approximately 6, the other of 3; he had marked a frequent isomorphism between elements from the different groups, yet did not therefore suggest any such modification of the existing atomic weights as would bring all elements under Dulong and Petit's law. Lenssen concentrated his attention on the discovery of his twenty triads.

Dumas' matured opinion,

Dumas at length, in 1858, ventured to publish that theory of elementary composition of which he had given hints in the Ipswich speech. On examination of the three and thirty best-determined atomic values—he gave particular attention to those of Marignac—he found that two and twenty of these were, within the limits of experimental accuracy, multiples of 1, eight were multiples of 0.5, and three of 0.25. With the qualification that the common unit accepted by Prout must be reduced by three-quarters of its value, he was now prepared to accept the latter's hypothesis. There was much more in these two papers which bore on this same question of the genesis of elements, much which might have been well written by Pettenkofer eight years before. Dumas' authority was great. Berzelius had been dead ten years, and even before, his accuracy had been impeached. Here, after forty-three years of unparalleled activity in the laboratory, was ratification of a theory

¹ Lothar Meyer, *Ostwald's Klassiker*, 66, p. 30.

a priori reasonable and wonderfully alluring. There was great excitement.

Three years later Jean Baptiste Stas, Professor of Chemistry in the military school at Brussels, published his *Recherches sur les rapports réciproques des poids atomiques*, and Prout's long-lived hypothesis was eliminated finally from the practical philosophy of the chemist. In paying a generous tribute to the genius of his great forerunner, Stas¹ writes: "The illustrious Berzelius consecrated a great part of his life to the fixing of chemical proportions. His work will remain an imperishable monument to his sagacity and genius. The minute and repeated control to which, in my hardiness, not to say temerity, I have submitted these, has convinced me that his analytical skill has never been surpassed, if ever it has been equalled." Such a monument as Berzelius raised to himself, Stas left behind to inform posterity of those gifts and virtues he had so praised in Berzelius. Stas was a pupil of Dumas, and began his work an almost convinced believer in Prout's principles. Yet a doubt remained, and he decided to bring the question to a judgment once and for all time final. After all, it was necessary to find but one exception to invalidate his whole faith; he would confine himself to a few crucial cases, and investigate the relations between the weights of the atoms of nitrogen, chlorine, sulphur, potassium, sodium, and of lead, remembering well the lessons taught by Dumas and Marignac, that the only means of establishing with exactitude and estimating accurately small differences in weight consisted in augmenting the quantities which produced them; so that these differences became much greater than the errors which observations entail. But the determination of these relations, involving as it did the synthesis, often repeated, and by the most varied processes, of silver chloride, sulphate and nitrate, of lead nitrate and sulphate, and analyses of potassium chlorate and silver sulphate, was too stupendous a task to win just appreciation from the reader, except by the most liberal generalization from the few experiments here so scantily described.

Stas' investigations.

¹ *Recherches*, p. 1.

Materials
used in
Stas' ex-
periments.

It was the question of the relation between the atomic weights of silver, chlorine, and potassium. This implied the synthesis of silver chloride, and subsequently the estimation of the chlorine content in potassium chloride by precipitation with silver. To do this Stas had balances varying in carrying power from 6 kilogs. sensitive to a milligramme, to 25 grms. sensitive to 0.03 milligramme; he had glassware previously heated to softening in magnesia, and therefore immune from that loss in weight which otherwise always occurred at high temperatures; he had water distilled, redistilled, and passed in vapour over red-hot copper oxide, to be received in a platinum condenser, and so pure that no residue, organic or otherwise, was left on evaporation; he had silver prepared by five different methods, and with the last refinements of intelligent patience, only to be employed after fusion on pure clay, rubbing with sand, refusion with solid potash, washing, again rubbing with sand, treating with boiling hydrochloric acid, washing with ammonia, with pure water, and finally heating to redness on plates of pure silver. He had potassium chloride prepared by four different methods, one of which consisted in fusing potassium chlorate in platinum crucibles. The potassium chlorate had itself been previously dissolved, filtered, treated twice with potassium sulphide to remove possible traces of iron and copper, recrystallized and washed with pure water, again and again recrystallized, and ever similarly washed; the chlorate then fused had yielded the chloride, from which possible traces of silica and alumina had been removed by stirring with a platinum brush, subsequently filtering through its own initial crystals, and by subsidence from the solution then made; the clear solution evaporated and fused with ammonium chloride had yielded what to Stas seemed a possibly pure preparation.

Stas' method.

To determine the composition of silver chloride, Stas synthesized the salt by four different methods. Here are the numerical details of one experiment where he had dissolved silver in nitric acid, and precipitated the chloride with gaseous hydrochloric acid, the whole being subsequently evaporated to dryness and fused in an atmosphere of the same acid. He

did not neglect to pass all nitrous fumes evolved through water, precipitate their silver content, and evaporate here, too, to dryness.

Silver in air	Silver in vacuo	Silver separated from nitrous fumes and weighed as chloride	Silver chloride in air	All the chloride in vacuo
108'553	108'549	0'0345	144'162	144'207 *

From this it followed that 100'000 grms. of silver yielded 132'849 grms. of the chloride. His other syntheses had given 132'843, 132'848, and 132'844 grms. of chloride respectively for 100'000 grms. silver used. The relation between 100 grms. of silver and the weight of potassium chloride it would precipitate he ascertained by dissolving silver in nitric acid in a stout stoppered glass vessel. Of the silver he took as much as Prout's hypothesis demanded for the decomposition of the chloride, which, in the nineteen experiments he conducted for the present issue, varied in weight between the limits of 22'3365 and 1'98565 grms. Any excess of silver was then precipitated with potassium chloride solution of known strength in a darkened chamber lighted with but a ray of yellow light. As the result of these nineteen experiments, Stas found that 100 grms. of silver decomposed potassium chloride varying in amount from 69'107 to 69'099 grms. And with much the same lavish expenditure of time and nerve, Stas then substituted common salt and ammonium chloride for the potassium chloride; and in yet another series of experiments, silver nitrate for metallic silver. But long before these last experiments reached their consummation Stas' work was done, and Prout's hypothesis lay shattered. Stas had calculated the gravimetric relations which must hold between silver and its various salts, or the salts of other metals, if Prout's hypothesis were true; he had then with unprecedented rigour tried the relationship in the laboratory. In the seven series of experiments he conducted, the differences between his experimental and Prout's hypothetical values were never less than three, though rising as high as fourteen times the difference between his maximum and minimum readings in the respective

series. And Stas concludes, "So long, then, as one will stand by experiment in establishing the laws which order matter, one should consider the law of Prout as a pure illusion, consider the undecomposed substances of our globe as things distinct and with no simple gravimetric relationship between them."

Yet the world was not quite convinced; Marignac, while admitting the brilliance of Stas' experiments, reserved to himself the right of still holding a tentative brief for Prout's law. He did not doubt Stas' facts, which, like those he had himself adduced, did certainly require explanation, if the decomposability of the element was still to be maintained; but might not such an explanation lie in a possible deviation from that law of constant proportions so confidently accepted since the time of Proust? Dumas, too, could still hug the idea that Prout's hypothesis was a philosophic verity to be ranked with those of Boyle and Gay Lussac, though sympathizing with Stas' work and admitting the cogency of his conclusions. But Stas was not the man to leave work only half done, and his experiments of the next five years¹ were all directed with the same minute exactitude as heretofore to turning the position of the over-cautious Marignac. In 1865 there remained no doubt that composition was independent of all physical circumstance, and that the gravimetric relationship between combining atoms was once and for all time fixed. His arguments, then, of 1869 were valid, and Prout's ghost finally laid.

Stas'
atomic
weights.

It was no difficult matter for Stas to calculate those atomic weights his results demanded—

O	=	8
Ag	=	107.943
Cl	=	35.46
K	=	39.13
Na	=	23.05
N	=	14.041
S	=	16.0371
Pb	=	103.453

¹ Cf. Stas, *Nouvelles Recherches sur les lois des proportions chimiques* (1865).

And this was in 1860. In modern times there have been none like to him, though some have trod worthily his footsteps.

Stas' atomic weights were merely what Humphrey Davy would long ago have called proportional numbers, and Gmelin, later, equivalents. The atomic weight of Berzelius was something of the past, conducive, perhaps, to pious reflection, but certainly not to practical results. Berzelius' initial misconception of Avogadro's hypothesis was partly accountable for this; partly, too, Dumas' want of imagination in interpreting the anomalous results obtained by his new vapour density apparatus. But chiefly was it due to a natural reaction among the younger chemists, tired of philosophy, anxious to do rather than talk. Hence the wonderful development of organic chemistry, a development too rapid for the wearied brain of Berzelius to cope with; hence the recent industry in analysis, for proportional numbers were indeed realities, and there were hints of an ascertainable relationship between them. Gmelin's rude philosophy was at the time most salutary, and Stas, with his carelessness of anything but certainty, could not but subscribe to it. But this scheme of mere equivalents was too brutal to satisfy. Chemistry was not confined to one school, and while most admitted the value of Gmelin's stoicism and many strove to imitate it, yet were these unwittingly moved by their preconceived notions of a loftier philosophy, perhaps that of Dalton, perhaps that of Berzelius, possibly that of Gerhardt. And the final result was deplorable. If one glances through the text-books current in the year 1860, he will find the formulæ for water written indifferently H_2O , HO , HO , or H_2O_2 , for marsh gas CH_4 , C_2H_4 , or C_2H_4 ; in one book $C_4H_4O_4$ suggested acetic acid, in another it could only mean fumaric or maleic acid. With more complex organic compounds the confusion was almost comic; Laurent¹ and Kekulé could either of them fill whole sheets with the varied formulæ for one substance culled from the pages of their contemporaries. Undoubtedly things were in a bad way. Formulation, which should have proved the most powerful instrument for the

The
atomic
theory
formulation
in
1860.

¹ Lothar Meyer, *Ostwald's Klassiker*, 30, p. 58.

spread of chemical truth, had become almost an absurdity, and this apparently from mere ignorance or selfish obstinacy. A meeting was convened at Karlsruhe by Welzien, Wurtz, and Kekulé; and here in September, 1860, there met in solemn conclave more than a hundred of the most famous chemists to consider what was to be done. There was great talk, much discussion, and some warmth. Odling deposed that since an element could have but one atomic weight, it could not have more than one; but Dumas would have it that two chemical sciences existed, the organic and inorganic, each with its own atomic philosophy, which greatly roused the Palermo professor Cannizzaro, who had long and deeply meditated the subject, and was ready to convert the world with a pamphlet, which in truth he did. Cannizzaro's eloquence was warmly received by those present, who were not, however, to be moved from the conclusions voiced by Hermann Kopp and Otto Erdmann, that one cannot agree on scientific questions, and that each investigator must be given his own way.

After the meeting was dismissed, copies of Cannizzaro's pamphlet were distributed; it is now a classic. One of them fell into the hands of Lothar Meyer: "I too got a copy, which I put in my pocket to read on my home journey. I read it again and again, and was astonished at the light which the writing threw on the most important points at issue. The scales fell from my eyes, doubt vanished, and a sense of the calmest certainty took its place." It was the vindication of the now ancient doctrine of Avogadro and Ampère that formed the thesis of this illuminating document; no new task to Cannizzaro, for his pamphlet was merely a reprint from an Italian journal of two years back, which had met the eye of few probably outside his own country. And long before the year 1858 Cannizzaro's pupils had received the advantage of their teacher's prescience. "My judgment from the history of chemical theory," says Cannizzaro, "as well as from the work of physicists, is that to reconcile all branches of chemical theory one must accept the theory of Avogadro and Ampère in all its fulness as a basis

Cf. *Ostwald's Klassiker*, 30.

for the determination of the weights and numbers of molecules. I make it my business to show that every consequence of this is in complete accord with all physical and chemical laws." Of elements and compounds, take such quantities as, vaporized, occupy the same volumes under the same conditions of temperature and pressure, and these will bear to one another the relation of their molecular weights. In compounds of the same element occupying similarly equal volumes, estimate the weights of any one element, and these will be found simple multiples of a value which must be taken as the atomic weight, and which in the case of a metal will always be found in agreement with that deduced from the law of Dulong and Petit. As in the case of carbon, one readily sees that it is quite unnecessary therefore to have previous knowledge of the molecular weights of the elements themselves. A comparison of the vapour densities of mercury and its chlorides at once explains the anomaly which puzzled Berzelius and Dumas; mercury in the state of vapour must exist as single atoms; similarly phosphorus and arsenic in aggregations of four. The long-vexed question of the formulation of silicon chloride is finally settled: consideration of its chlorine content demands the formula SiCl_4 , and the atomic weight for silicon of 28.

To the law of Avogadro and Ampère there were no exceptions.¹ Such anomalous cases as the vapour densities of ammonium chloride and phosphorus pentachloride, and the vapour density of sulphuric acid, urged by Mitscherlich and Bineau respectively against its accuracy, and sufficiently cogent to betray even the clear-sighted Gerhardt into a relaxation of his two-volume rule, were readily explainable to the unprejudiced mind. Deville's experiments were sufficient to show that ammonia and hydrochloric acid could exist together at a high temperature without combination; and it was much more probable that the other anomalous cases so lightly advanced by chemists were merely cases of decomposition on vaporization with recombination on cooling. So then the determination of vapour density offered final pronouncement

¹ Cf. *Ostwald's Klassiker*, 30, p. 44.

on the question of molecular weight; careful analysis would give at least an upper limit for atomic weight, while where doubt remained as to the number of atoms present in the molecule considered, there was great assistance offered by the discovery of Woestyn and Garnier, that the specific heat of atoms is uninfluenced by the state of combination; one had only to divide the molecular heat of the compound by the approximation 6.4 to arrive at the number required.

It would seem that there could be no longer any doubt as to the correct formulation of simple vaporizable substances; water must be H_2O , methane CH_4 , acetic acid $C_2H_4O_2$, hydrogen H_2 , mercury Hg ; and indeed it was not long before Cannizzaro's admirably timed pamphlet produced its effect. Seldom has intellectual revolution been effected without much clamour, jealousies, and backbitings; but here was one, and almost the profoundest that has affected the philosophical chemist. And how was it brought about? "To bring my students to the same conviction, I have made them travel the same road by which I have arrived, that of the historical investigation of chemical theories."

De Chan-
courtois'
natural
classifica-
..

With the acceptance of Cannizzaro's philosophy a comparative calm had settled on the minds of chemists; something great and of universal import had been achieved when from England, France, Germany, and Russia there could emanate chemical literature tended by a common atomic system. The carbon atom, at length revealed, was allowed such play that organic chemistry was rapidly assuming gigantic proportions; while to those who loved to muse on figures the philosophy of Proust, the speculations of Döbereiner and Pettenkofer, and the attitude of Dumas, suggested much lucubration. I have known men who, to while away the tedium of some lengthy sermon, will strive with the figures of the hymn-board to arrive at a coincidence or relation, and I have wondered at their initiative and industry. In such cases no one knows what will happen nor did de Chancourtois or Newlands know what would be the result of their play on Cannizzaro's numbers;

yet their achievements are historic. It was only after the final establishment of all the atomic weights that one could hope for any generalization covering all the elements conceived as atoms of known weight. Döbereiner had had to rest content with the discovery of his triads; Pettenkofer with his multiples of eight and of five; Dumas had finally divided the elements into three groups. But now, in 1863, Béguyer de Chancourtois¹ comes forward with his "natural classification of simple bodies or radicals." Almost all the elements are there arranged according to the magnitude of their atomic weights in sixteen perpendicular columns; and often it is that he finds elements in the same column exhibiting the very closest chemical analogies. But this system found no greater public than the conclave of the Paris Academy till again brought to light in 1889.

In the *Chemical News*, during the years 1863 and 1864, there appeared seven letters from the pen of John A. R. Newlands,² which had to do with "the relation among the equivalents"; their substance was a possible development of the field so industriously tilled by Dobereiner, Pettenkofer, and Dumas. Finally, on August 18, 1865, he gives as the result of his labour his "law of octaves," only previously hinted at. He adds a table—

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co } Ni }	22	Br 29	Pd 36	I 42
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 53
Ca 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd 83	Ba } V }	45
30 4	Al 11	Cr 19	Y 24	Ce } La }	33	U 40	Ta 46
5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
6	P 13	Mn 20	As 27	Di } Mo }	34	Sb 41	Nb 48
7	S 14	Fe 21	Se 28	Ro } Ru }	35	Te 43	Au 49
							Cs 51

—which shows how, with a few transpositions, elements

¹ Cf. Seubert, *Ostwald's Klassiker*, 68, p. 118.

² Cf. *The Periodic Law*, by J. A. R. Newlands.

belonging to the same natural group appear on the same horizontal line; how "numbers of analogous elements generally differ either by 7 or some multiple of 7; in other words, how members of the same group stand to each other in the same relation as the extremities of one or more octaves in music." This peculiar relationship he would term provisionally the "Law of Octaves." Undoubtedly the law of octaves was a considerable achievement. It was a perfectly fair attempt to find some other than a mere arbitrary system of classification, and was, moreover, immediately justified by its results. It was the courage of inspiration that allowed him to make his few transpositions; they were mostly unfounded, but at least served his purpose, by which we have so much profited. Newlands gave an account of his scheme to the Chemical Society in 1866. It was indeed very imperfect, and acute criticisms were offered; some of those present were even moved to humour.

Lothar
Meyer's
contribu-
tions.

So many had given their attention to this question of the relationship of the atomic weights; so much had been discovered, and so weighty was its issue, that Lothar Meyer necessarily devoted some pages of his *Die Modernen Theorien der Chemie*¹ to its consideration, and necessarily, with his mind, to its illumination. The first edition of this great work appeared in 1864, some years, therefore, after Cannizzaro had carried his reform; and Lothar Meyer was able, as no one before him, to apply to all the known elements these principles which Dobereiner, Pettenkofer, and others had so happily applied to the few. This was not yet, however; in 1864 he was content to point to the steady increment in atomic weight of elements belonging to the several groups, tetravalent, trivalent, divalent, or monovalent, an increment so constantly approximating to 16 or 48, that he was reminded of the constant difference of 22 in the molecular weights of homologous organic compounds. It might be that the elements were, like these compounds, aggregates of smallest particles of simpler matter; it certainly seemed reasonable, in view of

ascertained fact, to leave gaps between two elements differing by twice the accustomed increment. Here is an extract from the table to which he committed himself at this date—

	Tetravalent		Trivalent		Divalent
Difference =	<u>C = 12</u>	...	<u>N = 14.04</u>	...	<u>O = 16.00</u>
Difference =	16.5	...	16.96	...	16.07
	Si = 28.5	...	P = 31.0	...	S = 32.07
Difference =	$\frac{89.1}{2} = 44.55$...	44.0	...	46.7
	As = 75.0	...	Se = 78.8

—other vertical columns contained the monovalent halogen elements, the alkali metals and the divalent metals of the alkaline earths. Lothar Meyer's mind continued working on the atomic relationship, though he made no further official pronouncement till 1870. But in 1868,¹ on leaving Eberswalde, he left with his successor a table in which all the elements were arranged horizontally in the order of their atomic weights. There were sixteen vertical columns, made up of elements exhibiting close chemical and physical analogies, and room was left for elements hitherto undiscovered, but whose presence seemed demanded by obedience to what could no longer be regarded as coincidence. Yet Meyer for long received little credit for his activity. The following year the Russian Mendelejeff, seeking for some general principle by which he might order the elements in his new text-book, published a short statement in the *Zeitschrift für Chemie*, and a very long one in a Russian journal, of what has now come to be known as the Periodic law. In the year following Lothar Meyer too, in very condensed form, gave information to the public of his investigations; he offered a full table of atomic weights so nearly like Mendelejeff's that many accused him of plagiarism, yet so nearly like his own of 1868 that one would be almost justified in allowing him priority at least of conception. The

¹ Ostwald's *Klassiker*, 68, pp. 6-7.

question as to the real author of the Periodic law¹ was probably best solved by the Royal Society of London, who awarded Lothar Meyer and Mendelejeff the Davy medal simultaneously. In his new paper² Meyer arranged the elements in nine vertical columns, into the second of which fell the elements successively from boron to magnesium, elements showing a perfectly regular increase in valency. The elements on the same horizontal lines formed natural families, of which

I	II	III	IV	V	VI	VII	VIII	IX
← N=14.01	F=30.9			As=74.9		Sb=122.1		Bi=207.5
			V=51.2		Nb=93.7		Ta=182.2	
— O=15.96	S=31.98		Se=78		Te=128			—

are examples. Many spaces were necessarily left blank. But with the paper there was published a curve, the ordinates of which represented specific volumes, the abscissæ atomic weights. This curve wonderfully demonstrated not merely the dependence of physical property on atomic weight, but the very marked periodicity of this dependence. And now it was found that elements of similar physical properties other than their atomic volumes occupied similar positions on the similar sections of the curve. The curve having five peaks occupied by the most electro-positive elements, the metals of the alkalis, the halogen elements were found immediately before the peaks, the metals of the alkaline earths immediately after. The heavy malleable metals were all at the bottom of the several valleys. Lothar Meyer did not allow that his table, suggestive as it was, or his curve, so happily conceived to impress so many empirical observations, offered a key to the inter-relationship of the elements. But it at least offered a point of departure for the investigation of the inner nature of the hitherto undecomposed atoms, and, as it stood, might assist in correcting atomic weights doubtful by the breaks they caused in lines of coincidence otherwise so perfect. He would suggest a

¹ Cf. Seubert, *Ostwald's Klassiker*, 68.

² *Ibid.* ; also *Ann. Chem. Pharm.*, 7, p. 354.

re-examination of the weights of the tellurium, platinum, iridium and osmium atoms.

There was little in the paper of Lothar Meyer whose essence was not in Mendelejeff's¹ two papers, published the year previous, a fact duly noticed by the former. In the systematization of the elements for his new *Principles of Chemistry* Mendelejeff wished to be guided by something more certain than the mere instinct for the group; he would have some absolutely determinable quality by which to classify, and none seemed so irreproachable as the atomic weight which Cannizzaro's work had rendered available. And so he arranged the elements in six vertical columns, and found that by reasoned transposition here and omission there he was possessed of a table which well served his purpose of systematization. Elements exhibited a certain periodicity in their chemical and physical properties; those like to one another had atomic weights increasing by constant values or almost identical. He was led to prophesy the discovery of many new elements, and could immediately set about the correction of atomic values that caused irregularity. However, he would consider the end of his paper attained, as it affected the outside world, if he could turn the attention of chemists to the relationship between the atomic weights of dissimilar elements which had hitherto remained quite unheeded. And two years later, Mendelejeff had only the more confirmed himself in his opinion, which he again published in much greater extension. "I designate *the Periodic law*," he says, "the reciprocal relations between the properties of the elements and their atomic weights; these relations take the form of a periodic function." His table had taken a more developed form—

Mendelejeff's
period
law.

Series.	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
	P ₂ O ₅	RO	R ₂ O ₃	RH ₄ RO ₂	RH ₃ R ₂ O ₅	RH ₂ RO ₃	RH R ₂ O ₇	RO ₄
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	- = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	- = 68	- = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	? Yt = 88	Zr = 90	Nb = 94	Mo = 96	- = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 10
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	I = 127	
8	Cs = 133	Ba = 137	? Di = 138	? Ce = 140				
9	(—)							
10			? Er = 178	La = 180	Ta = 182	W = 184		Os = 195, Ir = 197, Pt = 198, Au = 199
11	(Au = 199)	Ag = 200	Tl = 204	Pb = 207	Bi = 208			
12				Th = 231		U = 240		

The eighth group he differentiated because of the facility with which osmium, ruthenium, and perhaps iron, form an oxide RO_4 . As points of similarity he marked their grey colour and difficult fusibility, their small atomic volumes, their power of condensing hydrogen and their permeability to it, the double cyanides they form with the alkali metals, and their ammoniacal salts. The atomic weights of unknown elements he obtained by taking the mean of the weights of what he called the *atom-analogues*. The atom-analogues of selenium were arsenic and bromine on the one hand, sulphur and tellurium on the other; its atomic weight should be $\left\{ \frac{75 + 80 + 32 + 125}{4} \right\} = 78$.

- All properties being functions of atomic weight, he could estimate similarly the physical and chemical character of any given element, known or unknown, from those of its atom-analogues. Mendelejeff did this for three elements, which he provisionally termed eka-aluminium, eka-silicon, and eka-boron. One has but to cast a glance on the following values to understand the glad acceptance finally rendered to the periodic law :—

EKA-ALUMINIUM¹

Suggested by Mendelejeff

Atomic weight, 68.
Specific weight, 6.0.
Atomic volume, 11.5.

GALLIUM

Discovered in 1875 by Lecoq de Boisbaudran

Atomic weight, 69.9.
Specific weight, 5.96.
Atomic volume, 11.7.

EKA-BORON

Suggested by Mendelejeff

Atomic weight, 44.
Oxide, Eb_2O_3 ; Sp. Gr., 3.5.
Sulphate, $\text{Eb}_2(\text{SO}_4)_3$.
Double sulphate not isomorphous with alum.

SCANDIUM

Discovered in 1879 by Nilson

Atomic weight, 43.97.
Oxide, Sc_2O_3 ; Sp. Gr., 3.864.
Sulphate, $\text{Sc}_2(\text{SO}_4)_3$.
Double sulphate, $3\text{K}_2\text{SO}_4 \cdot \text{Sc}_2(\text{SO}_4)_3$.
Crystallizes in fine columns.

Eka-silicon was finally discovered in 1886 by Winkler.

And here we may end this short, yet I hope conclusive as

¹ Cf. Seubert, *Ostwald's Klassiker*, 68, p. 133.

well as comprehensive, story. It is the story of some thousand years of almost fruitless labour, followed by two centuries of richest accomplishment. And we recognize connecting links between the two periods. Fire was an element to the ancients, a belief that profited them little; Stahl embraced it, renamed the element phlogiston, and gave soul to the work of the eighteenth century. The conception of atoms was another gift from the past; it likewise had proved valueless; but tried in the laboratory the conception became a theory, almost a certainty; and to-day we are furnished with intimate pictures of most complex matter. A mere glance at these pictures, and we are possessed with knowledge of the potentialities of the substances they portray; we know they are acid, or that they are alkaline; we know they are stable, or that they are unstable; we know, in fact, what Kekulé knew, what Lavoisier did not know. And even more intimate knowledge has come, and will come; we are linked with the sage of antiquity once again, by the common ideal of a one primordial substance; we find once again barrenness in the past, wonderful fertility in the present. It has been my pleasure to tell how this all came, pruning the story of what is not vital, striving to speak worthily of the thoughts and deeds of the great.

I hope it will be my readers' own fault if, having read carefully and generalized conscientiously, they do not in their future meditations see problems in a new and clearer light, and attack them with minds broadened by contact with those of their famous predecessors.

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THE END

